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CONTENTS

		PAGE
163.	Azulenes and related substances. Part II. A synthesis of azulene.—By Sukh Dev	729
164.	Dealcoholation reactions of the alkoxides of group IV elements.—By Ram Charan Mehrotra	731
165.	Studies on the behaviour of bi-univalent salts in aqueous solution. Part VIII. Nickel acetate.—By P. K. Jena, S. Aditya and B. Prasad ...	735
166.	Adsorption of water vapour on gelatine.—By J. C. Ghosh and B. P. Gyani	739
167.	Pechmann condensation. Part I. Condensation of orcinol and resorcinol with ethyl α-benzylacetoacetate.—By R. N. Usgaonkar, V. M. Thakor, G. V. Jadhav and R. C. Shah	743
168.	Kinetics of the oxidation of red phosphorus by iodine.—By G. S. Deshmukh and M. Venugopalan	747
169.	Synthetic insecticides. Part I.—By R. N. Chakravarti and R. C. Dhar ...	751
170.	Combination of acids and alkalies with gelatine.—By J. C. Ghosh and B. P. Gyani	755
171.	Oxalenediamidoxime. Part III. Estimation of palladium.—By P. R. Dasgupta	761
172.	Pechmann condensation. Part II. Condensation of 2:5-dialkylphenols with β-ketonic esters.—By R. N. Usgaonkar, V. M. Thakor, G. V. Jadhav and R. C. Shah	765
173.	Electrometric studies of rate of adsorption of acids by sugar charcoal from aqueous solutions.—By Kesho Dass Jain	772
174.	Ferric complexes of phenols. Part III. β-Resorcylic acid and pyrogallol.—By S. K. K. Jatkar and B. N. Mattoo	775
175.	Ferric complexes of phenols. Part IV. Pongamol and its estimation in karanja oil.—By S. K. K. Jatkar and B. N. Mattoo	779
176.	The component acids of refined karanja oil (*Pongamia glabra*, Vent).—By S. S. Gupta and C. R. Mitra	781
177.	Potentiometric studies in oxidation-reduction reactions. Part XV. Oxidation with potassium metaperiodate. Iodine bromide method.—By Balwant Singh and Apar Singh	786
178.	Azulenes and related substances. Part III. Studies in *cyclo*hept(f)-indene.—By Sukh Dev	789
179.	Search for new insecticides. Part VII.—By A. B. Sen and S. S. Parmar ...	801

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AZULENES AND RELATED SUBSTANCES. PART II. A SYNTHESIS OF AZULENE

By Sukh Dev

The action of diazomethane on indane under the influence of ultraviolet light gave an azulene precursor, which on dehydrogenation furnished azulene.

Of the various procedures, at present being utilised for the synthesis of azulenes, a widely used, though less unambiguous method makes use of the ring-expansion of aromatic compounds with diazoacetic ester (Braren and Buchner, *Ber.*, 1901, **34**, 982; *Ann. Reports*, 1947, **44**, 162; Pommer, *Z. angew. Chem.*, 1950, **62**, 281).

Diazomethane under the influence of ultraviolet light is capable of adding a methylene group on to an ethylenic linkage, thereby either expanding the system or producing a *cyclo*propane derivative (Doering *et al.*, *J. Amer. Chem. Soc.*, 1950, **72**, 2305; 1951, **73**, 876). When a solution of diazomethane in indane is exposed to ultraviolet radiations, nitrogen is slowly evolved and a compound, probably (I) or (II), is produced,

(I)

(II)

(III)

which on dehydrogenation furnished azulene (III). It is very likely that the reaction has a free radical mechanism and methylene bi-radicals are the active species (cf. Eister in "Newer Methods of Preparative Organic Chemistry", Interscience Publishers, New York, 1948, p. 558). When the reaction is carried out in ether solution, the yield of azulene, based on diazomethane, is very low, probably, due to the "cage effect" of the solvent (Remick, "Electronic Interpretations of Organic Chemistry", John Wiley and Sons, New York, 1949, p. 484).

By using diazoethane, it should be interesting to find out which methylazulene is produced, and work in that direction is in progress.

Experimental*

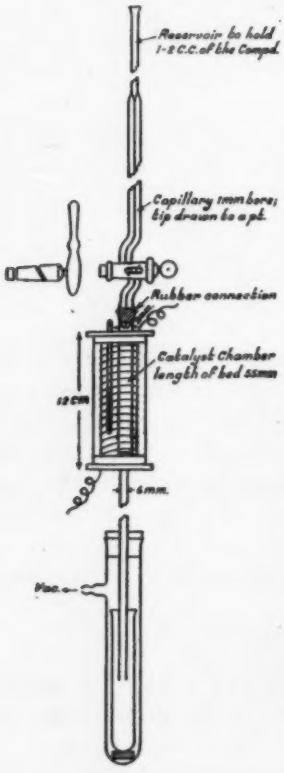
Indane.—Indene (80 g., b. p. 176°/684 mm.; n_D^{23}, 1.5749; f. p.+1°) was reduced over Adams PtO_2 catalyst (0.7 g.) at room temperature and a pressure of three atmospheres, without any solvent (cf. Dolliver, Gresham, Kistiakowsky and Vaughan, *J. Amer. Chem. Soc.*, 1937, **59**, 831). After the completion of hydrogenation (1½ hours), the reduced product was decanted off and another lot of indene (80 g.) was added to the same catalyst, which also took about the same time for hydrogenation and a third and fourth lot of indene were reduced in the same way over the same catalyst. The product was carefully fractionated through an efficient column; yield 410 g., b. p. 98°/70 mm., n_D^{25}, 1.5360. Indene (80 g.) was also reduced at 25°/684 mm. over $Pd(OH)_2$-$CaCO_3$ catalyst (15 g., Busch, *Ber.*, 1916, **49**, 1063; 1929, **62**, 1458) during 3 hours. Another lot of indene (80 g.) was hydrogenated over the

*All melting and boiling points are uncorrected.

same catalyst during the same period and worked up as above. This catalyst is easier to prepare and is more economical to use.

Azulene.—A solution of diazomethane (from 10 g. of nitrosomethylurea) in indane (50 c. c.) was prepared in the usual manner by covering the potassium hydroxide solution (10 g. in 20 c. c. of water) by this hydrocarbon, instead of ether. The deep yellow solution was dried over potassium hydroxide at 0° for several hours and then decanted off into a "Vitresol" flask. This was irradiated with an ultra-violet lamp, till the evolution of nitrogen ceased (26 hours). Indane was fractionated off and the residue (1.5 g.) was distilled from a suitable flask to give a straw coloured liquid, b.p. 70°-80°/14-15 mm., n_D^{25}, 1.5360, yield 1.0 g. (Found : C, 91.0 ; H, 8.9. $C_{10}H_{12}$ requires C, 90.9 ; H, 9.1 per cent).

FIG. 1


Reservoir to hold 1-2 C.C. of the Compd.
Capillary 1mm bore; tip drawn to a pt.
Rubber connection
Catalyst Chamber length of bed 55mm
12 cm
4mm.
Vac.

Dehydrogenation was carried out in the vapour phase under vacuum in the apparatus shown in Fig. 1 (cf. Nunn and Rapson, *J. Chem. Soc.*, 1949, 829 ; Anderson and Nelson, *J. Amer. Chem. Soc.*, 1951, **73**, 232). The catalyst chamber was packed with 30% palladium charcoal (0.5 g.) mixed with activated aluminia (0.5 g., −10,+20 mesh) ; two small plugs of freshly ignited asbestos were placed at either end to hold the catalyst in place. After assembling the apparatus, air was displaced with nitrogen and the dehydrogenation was carried out by allowing the material (700 mg.) to pass through the catalyst at 315°-325° and 30-40 mm. during 5 hours. The first few drops of the condensate were colorless, followed by a deep blue material. The product (575 mg.) was taken up in petroleum ether (30°-60°, 3 c. c.) and chromatographed over alumina (12 g.). The column was washed well with the same solvent ; two fractions (50 c. c., colorless ; 60 c. c., blue) were collected. The blue solution on removal of the solvent furnished the azulene as a blue solid (50 mg.). This was purified by sublimation at 30°-40°/1 mm. After two sublimations, the product (blue-violet plates) had m.p. 98-99° ; yield 40 mg. (Anderson and Nelson, *loc. cit.*, give m.p. 98-99°).

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DEALCOHOLATION REACTIONS OF THE ALKOXIDES OF GROUP IV ELEMENTS

By Ram Charan Mehrotra

It has been shown that on treatment of titanium and zirconium ethoxides and *iso*propoxides with hydrogen chloride, dichloride and trichloride derivatives of titanium and zirconium are respectively formed. The reaction of zirconium *n*-propoxide with hydrogen chloride gives an equimolecular mixture of the dichloride and trichloride zirconium derivatives. In contrast to the above, it has been shown conclusively that no reaction occurs between *n*-butyl orthosilicate and hydrogen chloride. These reactions throw fresh light on the reactivity of the tetrachlorides of these elements towards alcohols.

The reaction of alcohol with the tetrachlorides of silicon, titanium, zirconium and thorium can be represented by the following equations :

$$SiCl_4 + 4\ ROH \longrightarrow Si(OR)_4 + 4\ HCl\ ;$$

$$TiCl_4 + 3\ ROH \longrightarrow TiCl_2(OR)_2.ROH + 2\ HCl\ ;$$

$$2\ ZrCl_4 + 4\ ROH \longrightarrow ZrCl_3(OR).ROH + ZrCl_2(OR)_2 + 2\ HCl\ ;$$

$$ThCl_4 + 4\ ROH \longrightarrow ThCl_4.4\ ROH.$$

In view of the striking variation in the reactivity of the tetrachlorides of Group IV elements, it was considered of interest to investigate the reverse reaction of hydrogen chloride on the tetra-alkoxides of these elements.

Gerrard and Jones (*J. Chem. Soc.*, 1952, 1690) studied the reaction of hydrogen chloride on the butyl orthosilicate. They found that at 20° *n*-butyl orthosilicate did absorb hydrogen chloride corresponding to 0.77 mole of hydrogen chloride per mole of the alkoxide, but on aspiration and distillation, the original alkoxide was recovered almost unchanged in quantity. From these facts, they concluded that no reaction had occurred between the orthosilicate and hydrogen chloride. However, even if some reaction had occurred, the reaction mixture on aspiration and distillation would have given back the orthosilicate by the reverse reaction. Hence, the experimental evidence of Gerrard and Jones was indecisive. In the present investigation, a large excess of ethyl alcohol was added to the reaction mixture of hydrogen chloride and *n*-butyl orthosilicate and then nitrogen aspirated through the solution. If any monochloride derivative of silicon had been formed, then the formation of some monoethyltributyl orthosilicate would have occurred according to the following reaction :

$$SiCl(OBu)_3 + EtOH \rightleftarrows Si(OEt)(OBu)_3 + HCl.$$

No mixed alkoxide could be detected in the distillate from the product of the above reaction indicating that no reaction with the formation of chloride butoxide of silicon had occurred on passing hydrogen chloride through butyl orthosilicate.

On passing hydrogen chloride through titanium ethoxide or *iso*propoxide, the following reaction has been shown to take place :

$$Ti(OR)_4 + 2\ HCl \longrightarrow Ti(OR)_2Cl_2.ROH + ROH.$$

Similarly, zirconium *iso*propoxide has been shown to react with hydrogen chloride with the formation of trichloride mono-*iso*propoxide of zirconium which crystallises with two molecules of the alcohol :

$$Zr(OR)_4 + 3\,HCl \longrightarrow Zr(OR)Cl_3 \cdot 2\,ROH + ROH.$$

The reaction with zirconium ethoxide is similar to the above, but in the case of the *n*-propoxide of zirconium, the product consists of an equimolecular mixture of the dichloride and trichloride derivatives. The overall reaction in this case can be represented by the following equation :

$$2\,Zr(O\textit{n}\text{-}Pr)_4 + 5\,HCl \longrightarrow$$
$$Zr(O\textit{n}\text{-}Pr)Cl_3 \cdot 2\,\textit{n}\text{-}PrOH + Zr(O\textit{n}\text{-}Pr)_2Cl_2 \cdot \textit{n}\text{-}PrOH + 2\,\textit{n}\text{-}PrOH.$$

Thorium alkoxides have not been reported in the literature, but it can be safely inferred from the evidence presented in the above investigation that in their case, the reaction with hydrogen chloride would go even a stage further with the formation of the tetrachloride of thorium.

Experimental

Material.—*n*-Butyl orthosilicate was prepared by the action of *n*-butyl alcohol ('Analar', further purified by careful fractionation) on silicon tetrachloride, Reagent grade, and distilled twice, b.p. 95°/0.1 mm.

Titanium and zirconium alkoxides were prepared by the methods reported earlier (Bradley, Mehrotra and Wardlaw, *J. Chem. Soc.*, 1952, 2027, 4204, 5020). Each alkoxide was purified by distillation and zirconium *iso*propoxide was further purified by repeated crystallisation from *iso*propanol.

Throughout the investigations, all-glass apparatus with 'Quickfit' interchangeable joints was employed and very careful precautions were taken to exclude moisture.

Analytical Methods.—Silicon was estimated as silicon dioxide by decomposing the orthosilicate with concentrated sulphuric acid and igniting. Ethoxide and *iso*propoxide were estimated by determining the unchanged chromic acid, after a weighed sample of the alkoxide had been kept for 2 hours with an excess of the reagent (N-K_2CrO_4 in 12.5% H_2SO_4). They were quantitatively oxidised to acetic acid and acetone respectively under these conditions. However, it was found that *n*-propyl alcohol was oxidised further than propionic acid under the conditions, so the *n*-propoxide content was found empirically by comparing the chromic acid used up by a known weight of the alkoxide and a known weight of the alcohol under identical conditions.

Action of HCl *on* n-*Butyl Orthosilicate.*—Dry hydrogen chloride was passed for ½ hour through *n*-butyl orthosilicate (11.8 g.). Some heat was evolved and the final increase in weight was 1.1 g. Ethyl alcohol (40 g.) was added to the product and dry nitrogen bubbled through the solution for 3 hours. The volatile solvent was pumped off under reduced pressure and the product on distillation gave 11.1 g. of *n*-butyl orthosilicate boiling at 94°-96°/0.1 mm., leaving a residue (0.3 g.). [Found : Si, 8.75. Calc. for $Si(OBu)_4$: Si, 8.76 per cent].

Action of HCl *on Titanium* iso*Propoxide.*—HCl was bubbled through a solution of titanium *iso*propoxide (15.2 g.) in benzene (25 c.c.). After about 5 minutes, the temperature of the solution began to rise slowly in the beginning and finally the solution began to reflux with its own heat. The passage of HCl was continued until the solution began to cool down. It was allowed to stand guarded from atmospheric moisture for 12 hours, and next morning, the solvent was pumped off first on a water pump (pressure, 30 mm.) and finally under 0.5 mm. pressure for one hour giving a yellow solid (18.2 g.). This solid on analysis gave Ti, 14.2 ; Cl, 29.0 and *iso*PrO, 55.2%. Cl : Ti = 2.76 ; *iso*PrO, 2.97%. The analysis showed that the product was $TiCl_2(OisoPr)_2$. *iso*PrOH with some hydrogen chloride still adsorbed to it. This was confirmed on distilling the compound. On heating the compound (15.0 g.) under reduced pressure (8-9 mm.), the solid melted at a bath temperature of 60° and some volatile fraction came over at 38°-40°. Finally most of the liquid distilled over at 96°-100° giving a colorless liquid which solidified to give a white solid (10.9 g.). [Found : Ti, 20.2 ; Cl, 30.0 ; *iso*PrO, 49.5. Calc. for $TiCl_2(OisoPr)_2$: Ti, 20.2 ; Cl, 29.9 ; *iso*PrO, 49.9 per cent]. The solid was crystallised from *iso*propanol when colorless crystals were obtained which, when dried under reduced pressure, gave a white powder (11.3 g.). [Found : Ti, 16.1 ; Cl, 23.8 ; *iso*PrO, 59.5. Calc. for $TiCl_2(OisoPr)_2$. *iso*PrOH : Ti, 16.1 ; Cl, 23.9 ; *iso*PrO, 59.6 per cent].

Action of HCl *on Titanium Ethoxide.*—The reaction between titanium tetraethoxide and hydrogen chloride was similar to the above. Dry hydrogen chloride was passed through a solution of titanium ethoxide (14.1 g.) in benzene (25 c. c.). Much heat was evolved and from the product, the solvent was removed under reduced pressure when a yellow solid was obtained. On heating the solid under reduced pressure (8-9 mm.), it melted at a bath temperature of about 70° and some volatile fraction passed over at 40°-45°. The main fraction distilled at 120°-130° giving a slightly yellow liquid (8.7 g.) which solidified at room temperature. [Found : Ti, 22.99 ; Cl, 34.17 ; OEt, 42.8. Calc. for $TiCl_2(OEt)_2$: Ti, 22.93 ; Cl, 33.94 ; OEt, 43.13 per cent].

Reaction of Zirconium iso*Propoxide with* HCl.—A solution of zirconium *iso*propoxide [$Zr(OisoPr)_4$. *iso*PrOH, 6.5 g.] in benzene (28.7 g.) was treated with an excess of HCl. After a few minutes the temperature of the solution began to rise and finally reached about 45°. Bubbling of hydrogen chloride was continued until the solution cooled down to room temperature. The solvent was then removed under reduced pressure first at water pump (pressure 25 mm.) and then under 0.1 mm. pressure for eight hours, at a temperature not exceeding 40°, as it was found in a number of preliminary experiments that the product decomposed when heated to higher temperature even under highly reduced pressure. The viscous liquid, thus obtained, was set aside and slowly deposited a colorless crystalline solid which was washed twice with petroleum ether and finally dried for 5 hours at 40°/0.1 mm. The white powder obtained was analysed. [Found : Zr, 24.4 ; Cl, 29.3 ; *iso*PrO, 46.0. Calc. for $ZrCl_3$ ($OisoPr$). 2-*iso*PrOH : Zr, 24.2 ; Cl, 28.2 ; *iso*PrO, 47.0 per cent].

Reaction of HCl *with Zirconium Ethoxide.*—The reaction was similar to the above. The product, however, was a pasty solid which did not crystallise, nor did it become powder even after pumping off the solvent for 26 hours at 30°-40°/0.1 mm. The pasty solid was finally washed with petroleum ether and again dried at 40°/0.1 mm. for 6 hours. The product was analysed. (Found : Zr, 27.6 ; Cl, 31.71 ; EtO, 38.5. $ZrCl_3$ (OEt). 2EtOH requires Zr, 27.25 ; Cl, 31.78 ; EtO, 40.38 per cent].

Reaction of Zirconium n-*Propoxide with* HCl.—Zirconium *n*-propoxide (2.7 g.) was dissolved in about 40 c. c. of benzene and dry hydrogen chloride was bubbled through the solution. Heat was evolved in the reaction, but the solution cooled down to room temperature after passing hydrogen chloride for about 15 minutes. The solvent was pumped off for 6 hours at the room temperature when a little white solid crystallised out. The product was washed twice with petroleum ether and then dried under 0.1 mm. pressure for 6 hours at the room temperature, then for one hour at 40°-50° when 2.3 g. of a white powder was obtained. [Found : Zr, 25.53 ; Cl, 25.51 : PrO, 48.5. An equimolecular mixture of $ZrCl_3(O\textit{n}\text{-Pr}).2\textit{n}\text{-PrOH}$ and $ZrCl_2\text{-}(O\textit{n}\text{-Pr})_2.\textit{n}\text{-PrOH}$ requires Zr, 25.53 ; Cl, 24.61 ; PrO, 49.63 per cent].

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STUDIES ON THE BEHAVIOUR OF BI-UNIVALENT SALTS IN AQUEOUS SOLUTION . PART VIII. NICKEL ACETATE

By P. K. Jena, S. Aditya and B. Prasad

A study of the cells of the type : $Hg, Hg_2Ac_2 \left| \begin{matrix} NiAc_2, & HAc \\ c & c_1 \end{matrix} \right\| \begin{matrix} Salt \\ bridge \end{matrix} \left\| \begin{matrix} BaAc_2, & HAc \\ c & c_2 \end{matrix} \right| Hg_2Ac_2, Hg$ was undertaken using saturated and half saturated KCl bridge solution to eliminate liquid junction potential. Acetic acid was added to nickel acetate to suppress hydrolysis. Calculated amounts of acetic acid was added to barium acetate in order to make its p_H as that of nickel acetate solution at the corresponding concentration. Assuming barium acetate to be completely dissociated, the degree of dissociation of nickel acetate was calculated from the E. M. F. values of the above cells. The first stage of dissociation of nickel acetate ($NiAc_2 \rightarrow NiAc^+ + Ac^-$) was found to be complete. The dissociation constant, K, for the second stage of dissociation ($NiAc^+ \rightleftharpoons Ni^{++} + Ac^-$) was found to be 7.4×10^{-2}.

In the present paper, the E. M. F. of the cell,

$$Hg, Hg_2Ac_2 \left| \begin{matrix} NiAc_2, & HAc \\ c & c_1 \end{matrix} \right\| \begin{matrix} Salt \\ bridge \end{matrix} \left\| \begin{matrix} BaAc_2, & HAc \\ c & c_2 \end{matrix} \right| Hg_2Ac_2 \, . \, Hg$$

was measured to estimate the extent of ion association in nickel acetate solution.

Experimental

Nickel acetate was prepared by dissolving pure dry nickel hydroxide in acetic acid solution. Nickel hydroxide was prepared by adding an excess of caustic soda solution to a solution of nickel chloride. Nickel hydroxide thus obtained was freed from alkali by washing with distilled water and finally with doubled distilled water, in partial vacuum in a water-bath. Then the pure nickel hydroxide was heated in an air-oven at 98°-100° for hours till it was dry.

Nickel in the stock solution was estimated gravimetrically as nickel dimethylglyoxime. The strength of the solution was determined and found to be $0.9266M/5$. From this stock solution, the required solutions were prepared. The p_H of each of these solutions was measured by a Marconi p_H meter.

Barium in stock barium acetate solution was estimated gravimetrically as barium sulphate and from this solution 0.01, 0.02, 0.04, 0.06, 0.08 and 0.1 molar solutions were prepared. To each solution, before making the volume up to the mark, calculated amount of acetic acid was added to make the p_H of the solution same as that of nickel acetate solution at the corresponding concentrations. The p_H of the barium acetate solutions, thus prepared, was checked with the p_H meter mentioned above and found to have the expected values.

For setting up the cells, the process adopted was similar to that mentioned in Part VII of the series (this *Journal*, 1953, **30**, 633). The readings were taken

after 6 hours of setting up the cells. Even after 24 hours the change in the E. M. F. values was not more than 0.1 m.v. All the experiments were carried out at room temperature which varied from 30° to 32.5° and they were done in duplicate. Duplicate experiments agreed within 0.05 m.v. For a particular concentration the E. M. F. difference for saturated and half saturated KCl bridge did not differ by more than 0.25 m. v. For calculations only the E. M. F. values, when saturated KCl solution was used as bridge, were taken into consideration. The E. M. F. values were reduced to those values for 30° by using the equation :

$$\frac{E_t}{E_{30}} = \frac{273+t}{273+30}.$$

All the E. M. F. values are given in Table I (A, B).

TABLE IA

Cell : $Hg, Hg_2Ac_2 \left| \begin{matrix} BaAc_2, & HAc \\ c & c_1 \end{matrix} \right\| \text{half satd. KCl bridge} \left\| \begin{matrix} NiAc_2, & HAc \\ c & c_2 \end{matrix} \right| Hg_2Ac_2 . Hg.$

Conc. of $BaAc_2$ & $NiAc_2$ (molar).	Temp.	E. M. F.	Mean E. M. F.	Calc. E. M. F. at 30°.
0.01 0.01	31.5°	0.00140 volt 0.00135	0.00137 volt	0.001366 volt
0.02	32.0°	0.00205 0.00210	0.00207	0.002056
0.04	31.0°	0.00320 0.00325	0.00322	0.00321
0.06	32.0°	0.00390 0.00395	0.00392	0.003894
0.08	33.0°	0.00445 0.00445	0.00445	0.004406
0.10	31.0°	0.00480 0.00485	0.00482	0.004803

TABLE IB

Cell : $Hg, Hg_2Ac_2 \left| \begin{matrix} BaAc_2, & HAc \\ c & c_1 \end{matrix} \right\| \text{satd. KCl bridge} \left\| \begin{matrix} NiAc_2, & HAc \\ c & c_2 \end{matrix} \right| Hg_2Ac_2 . Hg.$

Conc. of $BaAc_2$ & $NiAc_2$ (molar).	Temp.	E. M. F.	Mean E. M. F.	Calc. E. M. F. at 30°.
0.01	31.0°	0.00150 volt. 0.00155	0.00152 volt.	0.001515 volt.
0.02	30.0°	0.00230 0.00235	0.00232	0.00232
0.04	31.0°	0.00310 0.00310	0.00310	0.003089
0.06	32.0°	0.00375 0.00375	0.00375	0.003725
0.08	32.5°	0.00445 0.00440	0.00442	0.004383
0.10	31.0°	0.00470 0.00475	0.00472	0.004703

TABLE II

Conc. of $NiAc_2$ soln.	a_{Ac^-}.	μ.	β.	K_2.
0.01 *M*	0.001597	0.0276	0.879	7.26×10^{-2}
0.02	0.0295	0.0525	0.812	7.14×10^{-2}
0.04	0.05373	0.0994	0.742	7.88×10^{-2}
0.06	0.07554	0.1430	0.692	7.57×10^{-2}
0.08	0.09553	0.1842	0.647	7.15×10^{-2}
0.10	0.1156	0.2256	0.628	7.47×10^{-2}
			Mean	7.41×10^{-2}.

DISCUSSION

Like other bi-univalent salts studied previously, we assumed at first that nickel acetate might be dissociating in two stages in aqueous solution.

$$NiAc_2 \rightleftarrows \overset{+}{NiAc} + \overset{-}{Ac}$$
$$\downarrow\uparrow$$
$$\overset{++}{Ni} + \overset{-}{Ac}$$

In this study the values of a' (activity of $\overset{-}{Ac}$ in $BaAc_2$), a (activity of $\overset{-}{Ac}$ in $NiAc_2$), α and β were found out in the manner explained in Part VII of this series (*loc. cit.*). For calculating the values of α and β, probable value of K_2 (dissociation constant for $\overset{+}{NiAc} \rightleftarrows \overset{++}{Ni} + \overset{-}{Ac}$) taken into consideration was 7×10^{-2}. This value of K_2 was obtained as follows.

It was found that for the lowest concentration (0.01*M*) the value of α was 50% more than the concentration of nickel acetate solution. Therefore it was taken into consideration that at this concentration the first stage of dissociation ($\overset{+}{NiAc_2} \rightarrow \overset{+}{NiAc} + Ac$) is complete. Now we have

$$NiAc_2 \rightarrow \underset{(1-\beta)c}{NiAc^+} + \underset{c}{Ac^-}$$
$$\downarrow\uparrow$$
$$\underset{\beta c}{\overset{++}{Ni}} + \underset{\beta c}{\overset{-}{Ac}}$$

knowing the values of 'c' (molar conc. of $NiAc_2$ solution), α, β, $\mu = 3c$ (rough ionic strength) and f_- (the activity coefficient of $\overset{-}{Ac}$, which was determined in the same manner as done in Part VII, *loc. cit.*), the value of β was determined from the relation

$$\frac{a}{f_- c} = 1 + \beta \qquad \ldots \quad (i)$$

From this rough value of β, a better value of μ was obtained from the relation,

$$\mu = c(1 + 2\beta) \qquad \ldots \quad (ii)$$

From this value of μ, the value of f was found out, and again, a more correct value for β was calculated from equation (*i*). This process of approximation was repeated till a constant value for μ was obtained. From the most correct value of β, the value for K_2 was calculated from the relation

$$K_2 = \frac{\beta c(1+\beta)}{(1-\beta)} f_{\pm} \qquad \ldots \quad (iii)$$

where $f_{\pm}$ is the activity of nickel ion. It was found out in a similar way, as was done in the paper mentioned earlier. Now the value of K_2 for the lowest concentration comes out to be 7.26×10^{-2}.

The values of α, calculated for all the concentrations studied, have been found to be near about one, which shows that in all the cases the first stage of dissociation is complete. Now, for all the concentrations studied, the values of μ, β and K_2 have been calculated in a similar manner as explained above for the lowest concentration and the values are given in Table II. The mean value for K_2 comes out to be 7.41×10^{-2}.

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ADSORPTION OF WATER VAPOUR ON GELATINE

By J. C. Ghosh and B. P. Gyani

Adsorption and desorption of water vapour with gelatine as a sorbent have been studied at low pressures (0-15 mm. Hg.) and ordinary temperatures (15°, 25° and 35°) in absence of air. The isotherms indicate a physical attachment of water to gelatine. They show hysteresis similar to that observed with an elastic adsorbent like cellulose. The isosteric heats of adsorption and desorption have been calculated from the isotherms. They are larger than the heats of condensation of water in bulk. It has been found that the temperature of evacuation of gelatine, so long as it is below 80°, has no effect on the nature of the isotherms. When gelatine was heated to 100° in vacuum, it had a tendency not to adsorb any water vapour due to some drastic changes in its structure.

Among the few published data on the sorption of water vapour by gelatine are those of Katz (*Koll.-Chem. Beih.*, 1917, **9**, 5), Wilson and Fuwa (*Ind. Eng. Chem.*, 1922, **14**, 913), and more recently of Sheppard, Houck and Dittmar (*J. Phys. Chem.*, 1940, **44**, 185). None of these workers seem to have taken care to purify the gelatine except Sheppard *et al.* and all of them carried out the measurements in presence of air. We therefore considered it desirable to carry out some measurements with highly purified gelatine and in complete absence of air. It becomes then easy to calculate the heats of sorption from the data so collected so as to arrive at a decision whether the combination corresponds to a mere condensation of water in the gelatine structure, or some other process.

Experimental

For measuring the amount of water taken up by the gelatine an apparatus similar to the sorption apparatus used by Gyani and Sinha (this *Journal*, 1952, **29**, 582) was constructed. Gelatine in the form of purified sheets from Merck was cut into thin slices about 5 mm. × 2 mm. and put into the sorption bulb. It was thoroughly evacuated at 40° intermittently for 4 days. The amount of sorption was measured by weighing the bulb directly. An Apiezon oil of low density and moderate viscosity was used in the differential manometer ; 15 mm. oil was found to exert the pressure of 1 mm. mercury by density measurements. The sorption bulb was kept at the desired temperature within ± 0.1° by keeping it immersed in suitable bath materials contained in a Dewar flask. Equilibrium was usually slowly attained even after the gelatine had been carefully evacuated ; 2 to 3 hours were usually required. It was noted that the sorption increased on continued flushing with vapour.

TABLE I

Heats of desorption (15°-35°).

x/m	...	0.04	0.05	0.06	0.07	0.08	0.09	0.10	0.12	0.14
Q (cal.)	...	13,728	15,480	15,718	16,658	17,411	16,545	16,392	15,230	14,359

TABLE II

Heats of adsorption (15°—35°)

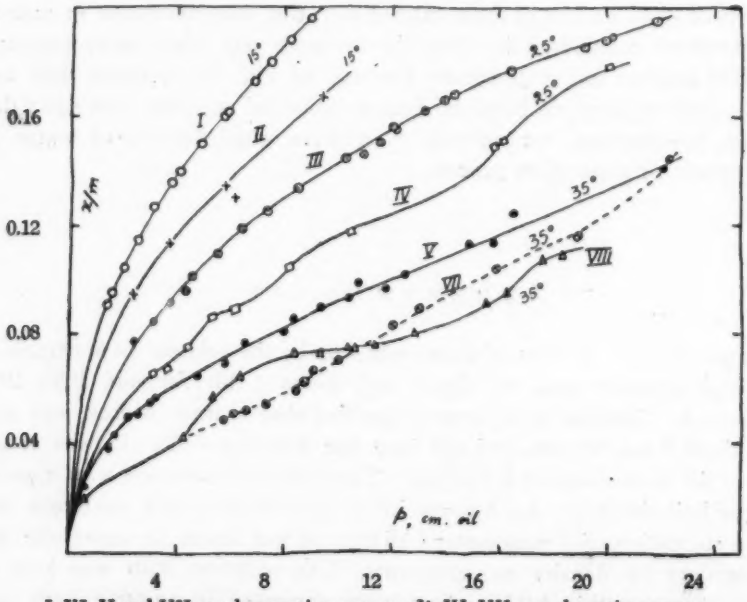
x/m	...	0.04	0.05	0.06	0.07	0.08	0.09	0.10	0.11
Q (cal.)	...	19,896	18,145	15,950	15,717	17,375	17,160	15,377	14,386

DISCUSSION

The results of these experiments are plotted as amount taken up by the gelatine x/m (g. per g. gelatine) against pressure p of water vapour in cm. oil (1 mm. oil = 0.067 mm. Hg) in Fig. 1. In some cases measurements have been taken both in adsorption

FIG. 1

Sorption isotherms.



I, III, V and VII are desporption curves ; II, IV, VII are adsorption curves (VII, first run).

and desorption. The desorption isotherms are smooth and occur higher than the adsorption isotherms.

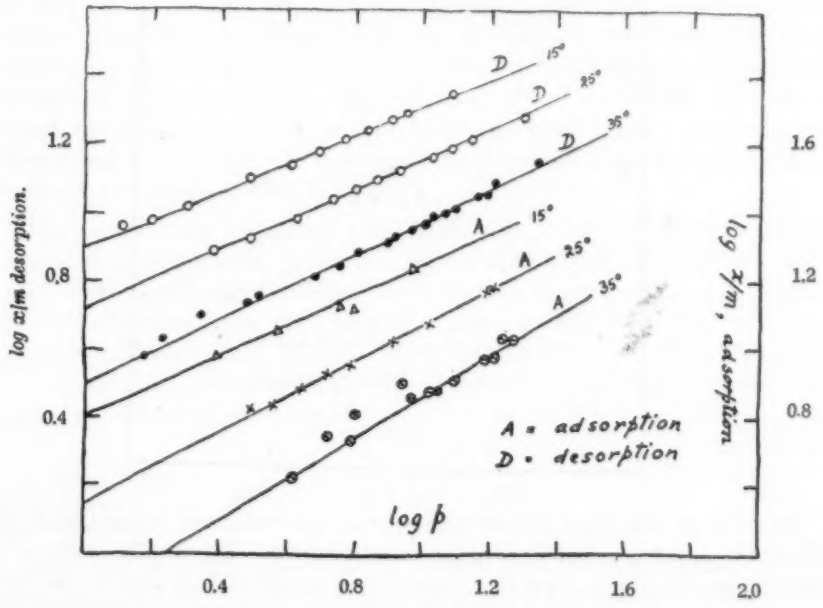
The graphs extend only to limited pressures and so it is difficult to say to what type they belong. However, a plot of log x/m against log$p$ (Fig. 2) gives quite satisfactory straight lines showing that the classical equation of adsorption,

$$x/m = k.p^{1/n}$$

is obeyed in the range of pressures studied. The plots of $\frac{p}{x/m}$ against p are far from straight lines so that obviously the isotherms are not of type I (Brunauer, "Adsorption of Gases and Vapours", Oxford University Press, 1943, p. 150). The combination appears to be quite definitely due to physical sorption.

FIG. 2

Plots of log x/m against log p.



To test this point further we have calculated the heats of combination from the isotherms at different temperatures, using the equation

$$\log \frac{p_1}{p_2} = \frac{-Q}{2.303\,R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

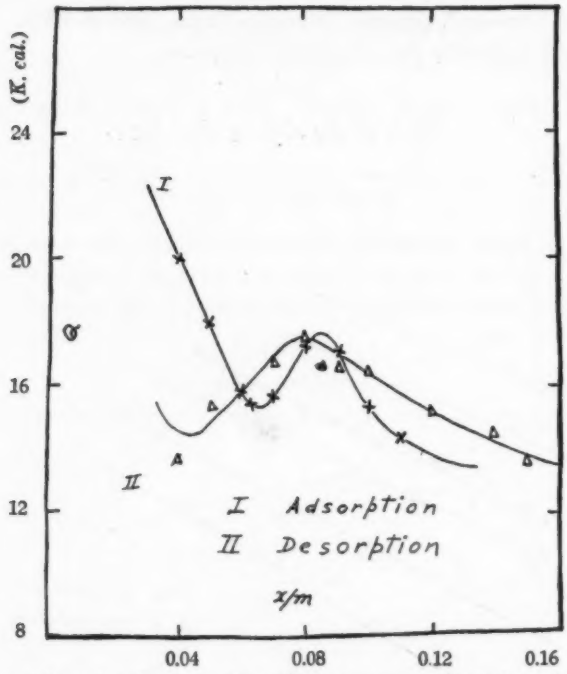
for fixed values of x/m. The results are summarised in Tables I and II. When Q is plotted against x/m, one gets graphs shown in Fig. 3. The shallow W is characteristic of sorption. The Q values are much higher than the heat of condensation of water in bulk, viz. about 10,000 cal./mol.

The isotherms of Fig. 1 show that there is large hysteresis between sorption and desorption. There is not much point in considering that the hysteresis in this

case originates in a capillary structure of gelatine. The results recall the hysteresis observed with cellulose, and perhaps its origin is also due to similar causes, *i.e.* coiling and uncoiling of the gelatine molecules at different stages of sorption, inhibiting a complete equilibrium in the case of adsorption due to space considerations.

FIG. 3

Isosteric heats of sorption : variation with amount sorbed.



To follow up this point further, the gelatine was subjected to heating in vacuum at different temperatures before sorption measurements. The results, some of which are incorporated in Fig. 1, show that there are no substantial changes in the isotherms so long as the gelatine is heated below 80°. The gelatine undergoes changes, possibly structural, above this temperature, and thereafter hardly sorbs any water even after continued contact with the vapour. These results recall the earlier observations of Alexander (*J. Amer. Chem. Soc.*, 1921, **43**, 434) who found that gelatine lost the power of disappearing in water if pre-heated to 130°. Possibly drastic changes in structure occur.

Further work is in progress. One of us (J. C. G.) thanks the Patna University for the grant of a research scholarship.

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PECHMANN CONDENSATION. PART I. CONDENSATION OF ORCINOL AND RESORCINOL WITH ETHYL α-BENZYLACETOACETATE

By R. N. Usgaonkar, V. M. Thakor, G. V. Jadhav and R. C. Shah

The condensation product of orcinol with ethyl α-benzylacetoacetate, described as 7-hydroxy-2 : 5-dimethyl-3-benzylchromone by Jacobson and Ghosh and as 7-hydroxy-3-benzyl-4 : 5-dimethylcoumarin by Baker, is now considered to be 5-hydroxy-3-benzyl-4 : 7-dimethylcoumarin. Resorcinol with the same ketonic ester has been found to give only one product, 7-hydroxy-3-benzyl-4-methylcoumarin, as observed by Chakravarti, contrary to the earlier claim of Jacobson and Ghosh.

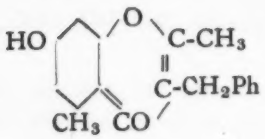
Jacobson and Ghosh (*J. Chem. Soc.*, 1915, **107**, 433) described the product obtained on condensation of orcinol with ethyl α-benzylacetoacetate in presence of concentrated sulphuric acid, as 7-hydroxy-2 : 5-dimethyl-3-benzylbenzo-γ-pyrone (I), to which later, Baker (*ibid.*, 1925, **127**, 2349) assigned the structure 7-hydroxy-3-benzyl-4 : 5-dimethylcoumarin (II) as the melting point of the product and its derivatives differed appreciably from those of the authentic specimens of the chromone and its derivatives, prepared by an unambiguous method. However, in view of the fact that the condensation of orcinol with β-ketonic esters generally leads to 5-hydroxycoumarin derivatives, the work was repeated (Dey, *ibid.*, 1915, **107**, 1606 ; Chakravarti, this *Journal*, 1931, **8**, 134).

When orcinol was condensed with ethyl α-benzylacetoacetate in presence of concentrated sulphuric acid according to the conditions of Jacobson and Ghosh (*loc. cit.*), only 3-methylindene-2-carboxylic acid, an internal condensation product of ethyl α-benzylacetoacetate, was isolated. Use of 80% sulphuric acid, however, furnished a product of m.p. 225-26°. This melting point of the product and the melting points of its derivatives differed considerably from those of the respective compounds by Jacobson and Ghosh (*loc. cit.*), as shown below.

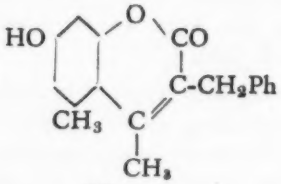
	Present work.	Jacobson and Ghosh.
Condensation product.	225-26°	177-78°
Acetyl derivative	115-16°	169°
Benzoyl derivative	169-70°	119-20°

The product failed to give a styryl derivative (Heilbron, Barnes and Morton, *J. Chem. Soc.*, 1923, **123**, 2559), but easily furnished a methoxycinnamic acid derivative by the method of Canter and Robertson (*ibid.*, **1931**, 1875) as modified by Shah and Shah (*J. Univ. Bombay*, 1938, **7**, 213), thus definitely establishing that it was a coumarin and not a chromone derivative. Out of the two alternative structures (II and III), it has been assigned the structure 5-hydroxy-3-benzyl-4 : 7-dimethylcoumarin (III) as it forms an insoluble yellow sodium salt with concentrated sodium hydroxide solution and in dilute solution it dissolves with a deep yellow colour without fluorescence, the characteristic property of a 5-hydroxycoumarin derivative (Dey, *loc. cit.*). The constitution also follows from the analogy to Pechmann condensation of orcinol with β-ketonic esters mentioned earlier. The same product was obtained when the condensation was carried out in presence of phosphorus oxychloride or anhydrous aluminium chloride in nitrobenzene.

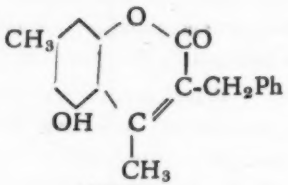
Jacobson and Ghosh (*loc. cit.*) have further claimed to have obtained two products during the condensation of resorcinol with ethyl α-benzylacetoacetate depending upon the proportion of concentrated sulphuric acid used : a product of m.p. 186°, which according to them is 7-hydroxy-2-methyl-3-benzylchromone, and another product of m. p. 224° which they suggest to be an addition product of the above chromone with resorcinol. Chakravarti (*loc. cit.*), however, during the condensation either in presence of sulphuric acid or phosphorus pentoxide could isolate only one product (m. p. 224°), to which he assigned the structure 7-hydroxy-3-benzyl-4-methylcoumarin. In the present case the condensation was carried out in presence of 80% sulphuric acid, phosphorus oxychloride (cf. Naik, Desai and Trivedi, (this *Journal*, 1929 6, 801) or anhydrous aluminium chloride in nitrobenzene, when only one product of m. p. 227-28° was obtained. Its analysis and molecular weight agreed with 7-hydroxy-3-benzyl 4-methylcoumarin. Further, it could not be broken up by refluxing with hydrochloric acid and the original compound was recovered unchanged. All these observations support the inference of Chakravarti that the product isolated is a 7-hydroxycoumarin derivative and not an addition product.



(I)



(II)



(III)

EXPERIMENTAL

Pechmann Condensation of Orcinol with Ethyl α-Benzylacetoacetate : 5-Hydroxy-3-benzyl-4 : 7-dimethylcoumarin (III)

1. *In presence of Sulphuric Acid.*—The condensation was first attempted according to the conditions given by Jacobson and Ghosh (*loc. cit.*). Anhydrous orcinol (3.0 g.) and ethyl α-benzylacetoacetate (5.5 g.) were treated with concentrated sulphuric acid (20 c. c.) and the reaction mixture was kept overnight at room temperature (*c.* 30°). It was poured over crushed ice and the white solid that separated was collected, washed and crystallised from acetic acid, when colorless needles of 3-methylindene-2-carboxylic acid, m. p. and mixed m. p. 201-202°, were obtained. Pechmann (*Ber.*, 1883, 16, 516) gives m. p. 199-200° ; Roser (*ibid.*, 1887, 20, 1574 ; *Annalen*, 1888, 247, 157) gives m. p. 200°. However, when 80% sulphuric acid was used instead of concentrated sulphuric acid in the above experiment and the crude product after washing with sodium bicarbonate solution crystallised from acetic acid, 5-hydroxy-3-benzyl-4 : 7-dimethylcoumarin was obtained in colorless needles, m. p. 225-26°. (Found : C, 76.85 ; H, 5.80. $C_{18}H_{16}O_3$ requires C, 77.14 ; H, 5.75 per cent).

Jacobson and Ghosh (*loc. cit.*) have described the condensation product as 7-hydroxy-2 : 5-dimethyl-3-benzylchromone, m. p. 177-78°, to which Baker (*loc. cit.*) suggested the constitution of 7-hydroxy-3-benzyl-4 : 5-dimethylcoumarin.

The product dissolves in dilute sodium hydroxide solution with a deep yellow colour without fluorescence. In 10% sodium hydroxide solution it first dissolves and immediately its deep yellow sodium salt is precipitated.

2. *In presence of Phosphorus Oxychloride.*—Phosphorus oxychloride (2.0 c. c.) was added to a mixture of orcinol (1.0 g.) and ethyl α-benzylacetoacetate (2.0 g.) and after slightly warming the mixture on a steam-bath (5-10 minutes), it was kept overnight at room temperature (*c.* 30°). It was digested with water and worked up as usual when the above 5-hydroxycoumarin, m. p. and mixed m. p. 225-26°, was obtained.

3. *In presence of Anhydrous Aluminium Chloride.*—To a mixture of orcinol (1.0 g.) and ethyl α-benzylacetoacetate (2.0 g.) a solution of anhydrous aluminium chloride (2.6 g., 2 mols.) in dry nitrobenzene (15 c. c.) was added and the mixture heated at 110°-115° for 2 hours in an oil-bath. It was cooled, ice and dilute hydrochloric acid added, and nitrobenzene was removed by steam-distillation. The black residue on crystallisation from acetic acid (charcoal) gave the above coumarin, m. p. and mixed m. p. 225-26°.

The acetyl derivative, prepared by acetic anhydride-pyridine method, was crystallised from alcohol (95%) in clusters of colorless needles, m. p. 115-16°. (Found : C, 74.56 ; H, 5.48. $C_{20}H_{18}O_4$ requires C, 74.53 ; H, 5.72 per cent). Jacobson and Ghosh (*loc. cit.*) give m. p. 169°.

The benzoyl derivative, prepared by benzoyl chloride-pyridine method, was crystallised from acetic acid in shining colorless cubes, m. p. 169-70°. (Found : C, 77.78 ; H, 5.62. $C_{25}H_{20}O_4$ requires C, 78.12 ; H, 5.20 per cent). Jacobson and Ghosh (*loc. cit.*) give m. p. 119-20°.

The *methyl* ether was prepared by adding dimethyl sulphate (1.0 c. c.) gradually to a cold solution of the coumarin (0.5 g.) in sufficient acetone (5 c. c.) and sodium hydroxide solution (10%, 10 c. c.) and crystallised after washing from rectified spirit in colorless shining needles, m. p. 157-58°. (Found : C, 77.49 ; H, 6.31. $C_{19}H_{18}O_3$ requires C, 77.55 ; H, 6.15 per cent).

2 : 6-*Dimethoxy*-4-β-*dimethyl*-α-*benzylcinnamic Acid.*—To the coumarin (1.0 g.) in acetone (10 c. c.), dimethyl sulphate (3.0 c. c.) was first added and then sodium hydroxide solution (10%, 30 c. c.) was gradually added with shaking and boiling the mixture under reflux. More dimethyl sulphate (in all 12 c. c.) and sodium hydroxide solution (10%, 100 c. c.) were alternately added, and the heating was continued for about two hours. It was cooled, filtered and the filtrate acidified with hydrochloric acid. The precipitate was treated with sodium bicarbonate solution. The product obtained on acidification of the bicarbonate solution was crystallised from dilute alcohol in colorless shining plates, m. p. 155-56°. (Found : C, 73.96 ; H, 7.21. $C_{20}H_{22}O_4$ requires C, 73.60 ; H, 6.74 per cent).

Pechmann Condensation of Resorcinol with Ethyl α-Benzylacetoacetate

7-*Hydroxy*-3-*benzyl*-4-*methylcoumarin.*—Resorcinol (3.0 g.), ethyl α-benzylacetoacetate (6.0 g.) and anhydrous aluminium chloride (7.5 g.) in dry nitrobenzene (30 c. c.) were heated in an oil-bath at 110°-115° for two hours. It was cooled, ice and hydrochloric acid added and steam distilled to remove nitrobenzene. The dark residue was crystallised from alcohol (95%) (charcoal) in colorless glistening prisms, m. p. 227-28°. [Found : C, 76.49 ; H. 4.92 ; M. W. (Rast), 276.1. Calc. for $C_{17}H_{14}O_3$: C, 76.69 ; H, 5.26 per cent. M. W. 266.0]. Chakravarti (*loc. cit.*) gives m. p. 224°. The same product was obtained when the condensation was carried out in presence of 80% sulphuric acid, phosphorus oxychloride or phosphorus pentoxide. No two products, as claimed by Jacobson and Ghosh (*loc. cit*), could be isolated depending upon the amount of sulphuric acid used. The acetyl derivative was crystallised from alcohol (75%), m. p. 169°. Jacobson and Ghosh (*loc. cit.*) and Chakravarti (*loc. cit.*) give m. p. 168°.

The coumarin (2.0 g.) was recovered unchanged when it was refluxed with concentrated hydrochloric acid (50 c. c.) in acetic acid (20 c. c.) for 11 hours.

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KINETICS OF THE OXIDATION OF RED PHOSPHORUS BY IODINE

By G. S. Deshmukh and M. Venugopalan

Kinetics of the oxidation of red phosphorus by iodine solution in KI has been studied. Using varying concentrations of iodine and the quantity of phosphorus between 0.01 g. and 0.02 g., the reaction has been found to be bimolecular over a temperature range of 20°-35°. The energy of activation and the temperature coefficient of the reaction have been calculated. Further work on the quantitative determination of red phosphorus by iodine is suggested.

The decolorisation of iodine solution in carbon disulphide and other organic solvents by red phosphorus was studied by Sestini and others (Sestini, *Gazzetta*, 1871, **1**, 323; Mellor, "A Comprehensive Treatise of Inorganic and Theoretical Chemistry", Vol. VIII, Longmans Green and Co., 1928, p. 785; Traxler and Germann, *J. Phys. Chem.*, 1925, **29**, 1119; Gordon and Krantz, *J. Amer. Pharm. Assoc.*, 1924, **13**, 609), who attributed it to its chemical adherence to the metalloid or/and to the formation of hydriodic and phosphorus acids. During studies in these laboratories on the use of various oxidants for the quantitative determination of red phosphorus (Deshmukh, *Analyst*, 1951, **76**, 604; Deshmukh and Sant, *Anal. Chem.*, 1952, **24**, 901) it was observed that the addition of a solution of iodine in potassium iodide to dry and purified samples of red phosphorus led to its gradual disappearance accompanied with a simultaneous fading of the colour of the solution. The rate of the above change was found to be measurably slow at ordinary temperatures. It was of interest therefore to study the kinetics of this oxidation process in some detail.

Experimental

Red phosphorus of B. D. H. laboratory reagent grade quality was purified by Buehrer and Schupp's method (*J. Amer. Chem. Soc.*, 1927, **49**, 9) and subsequently by the copper phosphide process (Deshmukh and Sant, *loc. cit.*). Its purity was checked by the magnesium pyrophosphate procedure. An accurately weighed quantity of the sample was introduced in a ground-glass stoppered Erlenmeyer flask containing a measured excess of standard iodine solution. This was maintained at a desired constant temperature for 30 minutes prior to the addition of phosphorus, and also during the course of subsequent observations, in an electrically heated thermostat fitted with an accurately calibrated automatic thermoregulator. The contents of the flask were swirled from time to time and an aliquot portion (5 ml.) of the clear supernatant solution was pipetted out carefully at different time intervals and titrated against standard thiosulphate. Series of experiments were carried out at different temperatures, viz., 20°, 25°, 30° and 35°, by varying the concentration of iodine and the weight of red phosphorus over a fairly wide range. A representative group of results is shown in Tables I-III.

TABLE I

Temp. = 20°. Wt. of P = 0.0112 g. Reaction mixture = 5 c. c.

A. 60 ml. of I_2 – $N/10$ (approx.).				B. 60 ml. of I_2 – $N/20$ (approx.).			
Time.	$N/20$-Thio.	$\log \frac{T_t (T_o - T\infty)}{T_o (T_t - T\infty)}$.	K.	Time.	$N/40$-Thio.	$\log \frac{T_t (T_o - T\infty)}{T_o (T_t - T\infty)}$.	K.
0 min.	9.02 c. c.	...	...	0 min.	8.95	...	...
10	8.95	0.0093	0.0003245	10	8.85	0.0032	0.0002076
25	8.85	0.0233	0.0003253	25	8.70	0.0083	0.0002154
45	8.70	0.0459	0.0003559	45	8.50	0.0154	0.0002220
90	8.45	0.0883	0.0003425	75	8.20	0.0269	0.0002327
180	8.05	0.1730	0.0003354	120	7.85	0.0420	0.0002271
300	7.60	0.3094	0.0003599	180	7.45	0.0617	0.0002224
∞	6.60	...	...	∞	3.55	...	...
		Mean K	0.0003406.			Mean K	0.0002212

TABLE II

Vol. of I_2 soln. = 60 ml.

Temp.	Wt. of P taken.	Conc. of I_2 added.	Conc. of thio.	Mean K.
20°	0.0112 g.	$N/10$	$N/20$	0.0003406
20°	0.0112	$N/20$	$N/40$	0.0002212
25°	0.0114	$N/10$	$N/20$	0.0006422
25°	0.0108	$N/20$	$N/40$	0.0010550
28°	0.0202	$N/10$	$N/20$	0.0010518
30°	0.0094	$N/20$	$N/20$	0.0050200
30°	0.0108	$N/20$	$N/40$	0.0022060
30°	0.0208	$N/10$	$N/20$	0.0013560
35°	0.0106	$N/10$	$N/20$	0.0026325
35°	0.0106	$N/20$	$N/40$	0.0031840

TABLE III

Temp. $T_1 - T_2$	Conc. of iodine.	K_1.	K_2.	Temp. coeff. K_2/K_1.	Energy of activation $\frac{2.303 \log_{10} \frac{K_2}{K_1} \times R \times T_1 \times T_2}{T_2 - T_1}$.
20-30°	$N/10$	0.0003406	0.0013560	3.980	24370 g. cals.
25-35°	$N/10$	0.0006422	0.0026325	4.101	25870 ,,
25-35°	$N/20$	0.0010550	0.0031840	3.018	20250 ,,

The energy of activation and the temperature coefficient were calculated from the values obtained for K at different temperatures T_1 and T_2 as indicated in Table III.

FIG. 1

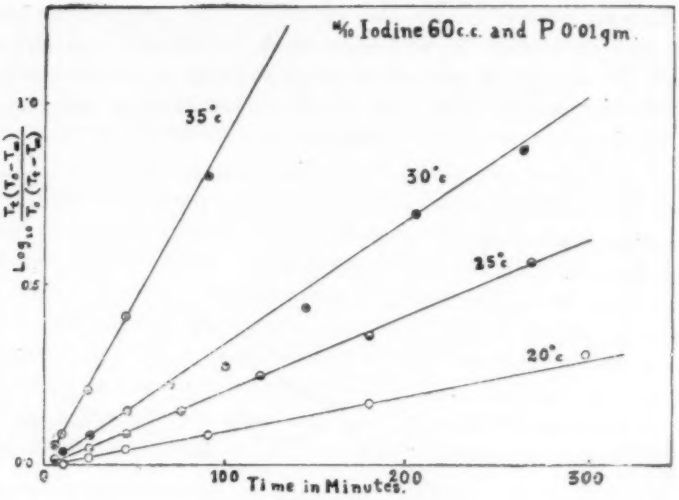
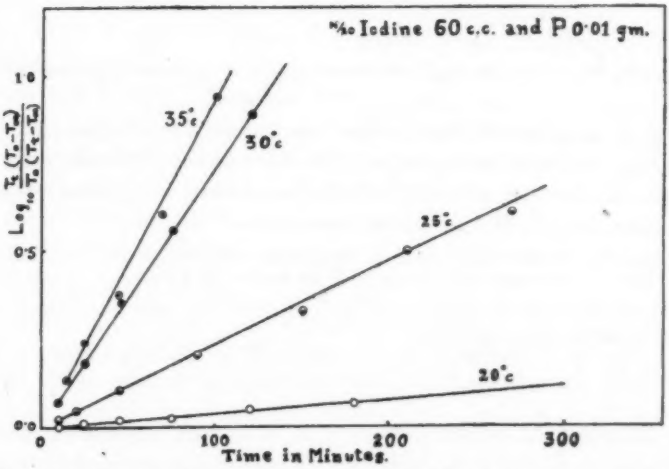


FIG. 2



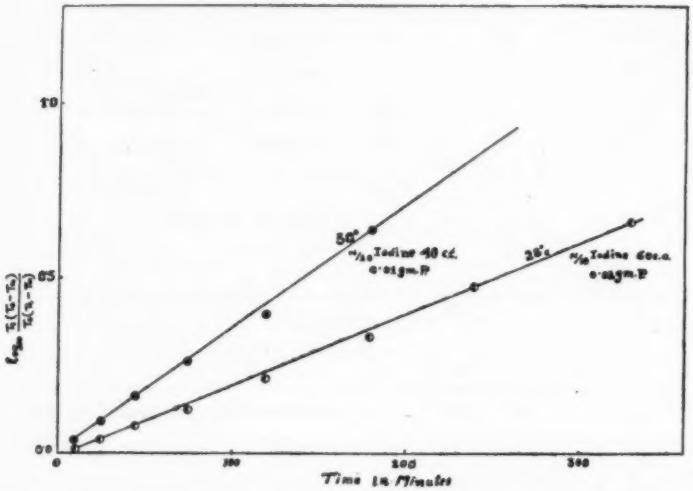
From the initial titre value of iodine and that obtained at various time intervals during the course of the oxidation, the order of reaction was calculated by the integration method. Under the given operative conditions the value of K was found to be constant and within limits of experimental error according to the following equation :

$$K=\frac{2.303}{t\,T_\infty}\log_{10}\frac{T_t(T_0-T_\infty)}{T_0(T_t-T_\infty)}$$

where T_0 = initial conc. of I_2 ; T_t = conc. of I_2 at time t ; T_∞ = conc. of I_2 at time ∞ and t = time in minutes.

The results (Tables I-III) therefore show that the oxidation of red phosphorus by iodine in KI is an overall bimolecular reaction. The temperature coefficient of the reaction and its energy of activation were calculated from the values of K obtained at 20°, 25°, 30° and 35° with $N/10$ iodine and 0.01 g. of phosphorus approximately. These correspond to 4.101, 3.98 and 25,870 and 24,370 g. cals. respectively.

FIG. 3



A series of experiments were carried out in which the difference in the quantity of iodine added initially to a given weight of P and that left over after its complete disappearance, *i.e.*, the titre value at infinite time, served as a measure of the quantity of iodine required for the oxidation reaction.

These results show that for a complete oxidation under the above experimental conditions the molecular ratio of P to iodine is 1 : 4.

From these data the formation of both phosphorus and phosphoric acid may be inferred according to the reaction :

$$2P+4I_2+7H_2O \longrightarrow H_3PO_3+H_3PO_4+8HI$$

Incidentally this supports the observations of Sestini and other workers (*loc. cit.*).

It may, however, be pointed out that in a system containing small quantities of P suspended in iodine in KI, it is difficult to analyse or/and isolate unmistakeably the presence of various oxidation products of phosphorus which ordinarily show a remarkable similarity in their chemical properties.

The possibility of adopting the above oxidation reaction for the quantitative determination of red phosphorus is being investigated.

Sincere thanks of the authors are due to Professor S. S. Joshi, for facilities and interest in the work.

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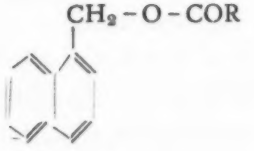
SYNTHETIC INSECTICIDES. PART I

By R. N. Chakravarti and R. C. Dhar

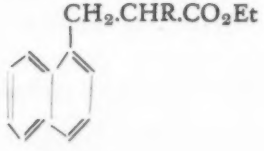
A number of new non-halogenated α-menaphthyl esters have been prepared as potential insecticides.

Amongst non-halogenated insecticides, compounds containing the benzyl group occupy a distinct position, viz., benzyl alcohol, benzyl acetate and notably benzyl benzoate and benzyl thiocyanate. In analogy with these derivatives it was thought desirable to prepare a series of esters containing the menaphthyl group and to screen these for their insecticidal character. The menaphthyl group may be regarded as a benzyl group with a fused benzene ring. Thus the menaphthyl group may be expected to retain some of the properties of both benzyl and naphthyl groups, and so menaphthyl esters may be expected to have pronounced insecticidal properties as both benzyl and naphthyl groups are associated with such properties.

α-Menaphthyl acetate was prepared by Manske and Ledingham (*Canadian J. Res.*, 1939, **17B**, 17) by heating α-chloromethylnaphthalene with potassium acetate in acid solution. As acetic acid cannot be used for the preparation of other menaphthyl esters, the usual method of heating the potassium salt of the corresponding acid with α-chloromethylnaphthalene in presence of absolute ethanol was tried but failed to give satisfactory results, the yields being mostly very low and the products invariably gave a positive Beilstein test indicating the presence of halogen in the product. These difficulties were obviated by adopting a direct heating of the potassium salt of the acid with α-chloromethylnaphthalene in an oil-bath at 150°-170° in presence of a little of the corresponding free acid. The results obtained by this method were usually satisfactory as regards yield and the products in most cases did not respond to the Beilstein test.



(I)



(II)

For preparation of menaphthyl derivatives of the type (II, R=CO_2Et, CN and COMe), condensation of α-chloromethylnaphthalene with ethyl malonate, ethyl cyanoacetate and ethyl acetoacetate was carried out in the usual way by heating the reactants in absolute ethanolic solution in presence of sodium ethylate. Comparative results of assay of these compounds for their insecticidal character will appear elsewhere.

EXPERIMENTAL

α-Chloromethylnaphthalene required for the work was prepared by following the method as described in "Organic Reactions" (Vol. I, p. 70; cf. Cambron, *Canadian J. Res.*, 1939, **17B**, 12).

The product obtained was carefully fractionated under reduced pressure. It yielded a forerun of unreacted naphthalene. The main fraction distilled at 130°-135°/6mm. From the high boiling fraction some 1 : 5-*bis*-chloromethylnaphthalene could be obtained, which crystallised from benzene in colorless prisms, m.p. 145°.

General Method of Preparation of the Menaphthyl Esters.—An intimate mixture of the potassium salt of the acid (1.1*M*), the free acid (0.1*M*) and α-chloromethylnaphthalene (1*M*), in the absence of any solvent, was heated in an oil-bath for 16 hours using a vertical glass tube as an air condenser, the temperature of the bath being raised from 150° to 170° during the period. The cooled product was diluted with water and taken up in ether. The ethereal solution was washed with a saturated solution of sodium bicarbonate and finally with water. It was dried over anhydrous calcium chloride and the ether was evaporated. The residual oil was finally purified by fractionation under reduced pressure.

The potassium salt of the acid required for the above preparation was most conveniently prepared by neutralising an aqueous solution of the appropriate acid with potassium hydroxide solution using phenolphthalein as an indicator. The solution was evaporated on the water-bath and then in an evacuated desiccator. The crude potassium salt obtained in this way was directly used for the above preparation.

The following α-menaphthyl esters were prepared by the general method described above.

I. *α-Menaphthyl Esters of Monocarboxylic Aliphatic Acids :* (*i*) *α-Menaphthyl Propionate* (I, R = C_2H_5).—Colorless liquid, b.p. 174°/5 mm., yield 80%. (Found : C, 78.5 ; H, 6.4. $C_{14}H_{14}O_2$ requires C, 78.5 ; H, 6.5 per cent).

(*ii*) *α-Menaphthyl Butyrate.*—Colorless liquid, b.p. 188°/5 mm., yield 65%. (Found : C, 78.7 ; H, 6.9. $C_{15}H_{16}O_2$ requires C, 78.9 ; H, 7.0 per cent).

(*iii*) *α-Menaphthyl Laevulate* (I, R = $CH_2.CH_2.COCH_3$).—Colorless liquid, b.p. 215°/5 mm., yield 85%. (Found : C, 75.1 ; H, 6.0. $C_{16}H_{16}O_3$ requires C, 75.0 ; H, 6.2 per cent). With semicarbazide hydrochloride and sodium acetate in aqueous ethanol it gave a crystalline semicarbazone which separated from 90% ethanol in feathery needles, m.p. 182-83°. (Found : C, 65.1 ; H, 5.8 ; N, 13.7. $C_{17}H_{19}O_3N_3$ requires C, 65.1 ; H, 6.0 ; N, 13.4 per cent).

(*iv*) *α-Menaphthyl Crotonate* (I, R = CH : $CH.CH_3$).—Light yellow oily liquid, b.p. 170°/4-5 mm., yield 65%. (Found : C, 80.0 ; H, 6.3. $C_{15}H_{14}O_2$ requires C, 79.6 ; H, 6.2 per cent).

II. *α-Menaphthyl Esters of Monocarboxylic Aromatic Acids : (i) α-Menaphthyl Benzoate* (I, R=C_6H_5).– Colorless liquid, b.p 211°/4-5 mm., yield 65%. (Found : C, 82.2 ; H, 5.2. $C_{18}H_{14}O_2$ requires C, 82.4 ; H, 5.3 per cent).

(ii) α-Menaphthyl Phenylacetate (I, R=$CH_2.C_6H_5$).—Light yellow viscous liquid, b.p. 212°/4-5 mm., yield 85%. (Found : C, 82.4 ; H, 5.6. $C_{19}H_{16}O_2$ requires C, 82.6 ; H, 5.8 per cent).

(iii) α-Menaphthyl Cinnamate (I, R = CH : CH. C_6H_5).– Brown viscous liquid, b.p. 245°/6 mm., yield 65%. It solidified on keeping and crystallised from absolute ethanol in needle-shaped crystals, m.p. 68-69°. (Found : C, 83.3 ; H, 5.7. $C_{20}H_{16}O_2$ requires C, 83.3 ; H, 5.6 per cent).

III. *α-Menaphthyl Esters of Hydroxy and Phenolic Aromatic Acids : (i) α-Menaphthyl Mandelate* [I, R = CH(OH).C_6H_5].—Light yellow viscous liquid, b.p. 225°/7 mm., yield 40%. (Found : C, 78.3 ; H, 5.4. $C_{19}H_{16}O_3$ requires C, 78.1 ; H, 5.5 per cent).

(ii) α-Menaphthyl Salicylate (I, R = C_6H_4OH).—Viscous liquid with a characteristic smell, b.p. 230°/5 mm., yield 40%. (Found : C, 77.4 ; H, 4.8. $C_{18}H_{14}O_3$ requires C, 77.7 ; H, 5.0 per cent).

IV. *α-Menaphthyl Esters of Polybasic Acids : (i) Di-α-menaphthyl Maleate.* —Brown viscous liquid, b.p. 170°/6mm., yield 2% (Found : C, 78.6 ; H, 4.8. $C_{26}H_{20}O_4$ requires C, 78.8 ; H, 5.0 per cent).

(ii) Di-α-menaphthyl Adipate.—Thick yellow liquid, b.p. 240°/6mm., yield 10%. (Found : C, 78.7 ; H, 6.0 $C_{28}H_{26}O_4$ requires C, 78.9 ; H, 6.1 per cent).

(iii) Di-α-menaphthyl Phthalate.—Viscous liquid, b.p. 240°/6 mm., yield 8%. It partly solidified on keeping, m.p. 170°. (Found : C, 80.4 ; H, 4.9. $C_{30}H_{22}O_4$ requires C, 80.7 ; H, 4.9 per cent).

(iv) Di-α-menaphthyl Succinate.—Gummy liquid, b.p. 240°-260°/4mm., yield 20%. It solidified on cooling and crystallised from absolute ethanol in needle-shaped crystals, m.p. 129°. (Found : C, 78.6 ; H, 5.7. $C_{26}H_{22}O_4$ requires C, 78.4 ; H, 5.5 per cent).

General Method of Preparation of α-Menaphthyl-substituted Malonic, Cyanoacetic and Acetoacetic Esters

The ester (ethyl malonate, ethyl cyanoacetate, ethyl acetoacetate) (0.1*M*) was added to a cold solution of sodium (0.1 atomic proportion) in absolute ethanol (35 c. c.). To the sodio salt obtained in this way was added α-chloromethylnaphthalene (0.1 *M*) and left overnight. It was refluxed on a water-bath for ten to twelve hours and the excess of ethanol was then removed under reduced pressure. The residual oil was taken up in ether, washed with water, dried over sodium sulphate and the ether evaporated. The product was then purified by fractionation under reduced pressure.

The following α-menaphthyl-substituted esters were prepared by the general method described above.

(*i*) *Ethyl α-Menaphthylmalonate* (II, R = CO_2Et).—Colorless liquid, b. p. 200 /6 mm., yield 45%. (Found : C, 72.0 ; H, 6.5. $C_{18}H_{20}O_4$ requires C, 72.0 ; H, 6.7 per cent).

(*ii*) *Ethyl α-Menaphthylcyanoacetate* (II, R = CN).—Light yellow liquid, b.p. 185°/6 mm., yield 15%. (Found : C, 75.6 ; H, 6.0. $C_{16}H_{15}O_2N$ requires C, 75.9 ; H, 5.9 per cent).

(*iii*) *Ethyl α-Menaphthylacetoacetate* (II, R = $CO.CH_3$).—Colorless liquid, b.p. 190°/6mm., yield 35%. (Found : C, 76.0 ; H. 6.9. $C_{17}H_{18}O_3$ requires C, 75.5 ; H, 6.7 per cent).

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COMBINATION OF ACIDS AND ALKALIES WITH GELATINE

By J. C. Ghosh and B. P. Gyani

Combinations of a number of acids (HCl, H_2SO_4 and $ClCH_2COOH$) and alkalies (NaOH and KOH) with gelatine at different temperatures have been studied by a potentiometric method. It is found that alkalies are positively adsorbed at all temperatures, and the temperature coefficient of the combination is negative. The acids, on the other hand, are negatively adsorbed except at very low concentrations, and the temperature coefficient is again negative. The heats of combination of gelatine and the alkalies have been obtained from the graphs of combination at different temperatures. The values show that the initial combination is far from a simple neutralisation, though at later stages it may be so. Some tentative views have been expressed about the negative combination with acids and differences in behaviour towards NaOH and KOH.

The combination of HCl and NaOH with gelatine has been studied by many workers who have used different methods. Most of them appear to hold the view that there is a maximum combining capacity of gelatine for these, and some of the results are summarised below in Table I.

Table I

Maximum combining capacity of gelatine for acids and bases

(g. equiv./g. gelatine $\times 10^5$).

	Max. combining capacity.	Method of measurement.	References.	
HCl,	130	Electrometric titration	Proctor & Wilson	(1)
	70	Indicator "	Bracewell	(2)
	119	Catalytic action of H^+	Wintgren & Krüger	(3)
	300	Electrometric titration	Lloyd & Mays	(4)
	92	" "	Hitchcock	(5)
	92	Diffusion potential	Ferguson & Bacon	(6)
	48-76	Titration	Oakes & Davis	(7)
NaOH,	130	Electrometric titration	Proctor & Wilson	(1)
	93	" "	Hitchcock	(8)

References: (1) *J. Chem. Soc.*, 1916, **109**. 307. (2) *J. Amer. Chem. Soc.*, 1919, **41**, 1511. (3) *Kolloid Z.*, 1921, **28**, 81. (4) *Proc. Roy. Soc.*, 1922, **93B**, 69. (5) *J. Gen. Physiol.*, 1922, **4**, 733. (6) *J. Amer. Chem. Soc.*, 1927, **49**, 1921. (7) *Ind. Eng. Chem.*, 1922, **14**, 706. (8) *J. Gen. Physiol.*, 1931, **15**, 125.

One notes that the maximum combining capacities are not quite reproducible and occasionally the discrepancies are large. Particularly divergent values were obtained by Friedman, Klemm and Thompson (*J. Phys. Chem.*, 1939, **43**, 1136) in extending the study to other acids and bases (7700×10^{-5} for oxalic acid; 453×10^{-5} for ammonia).

Lloyd and Mays (*loc. cit.*) found breaks in the graphs of HCl combined against its concentration, which they interpreted as successive combinations with amino, imino and amido groups. Most other workers report that the graphs are smooth. Thus, Izaguire (*Kolloid Z.*, 1922, **32**, 47) finds that the HCl combined (y) and the original concentration of the acid in the mixture with the gelatine sol (x) have the

relation $\log y = a + b \log x$, whence they conclude that the combination corresponds to adsorption, though the equation used is not quite that for adsorption.

To further clear up the views regarding the observation of Lloyd and Mays, Hoffman and Gortner chose prolamines, which are better defined compounds than gelatine, and using alcoholic solutions showed that in the p_H range 2.5–10.5 the combination of acids and alkalies was stoichiometric, but beyond this range it appeared to be governed by adsorption. The present investigations have been undertaken under these controversial circumstances to find out (*i*) what is the nature of action of acids and alkalies on gelatine, (*ii*) what information may be had from this study on the state of gelatine itself in the sol, and (*iii*) whether the conclusions of Hoffman and Gortner (Colloid Symposium Monograph II, Chem. Catalog Co, New York, 1925) may be extended to aqueous gelatine sols.

EXPERIMENTAL

For these experiments Merck's gelatine was purified as described in a previous paper (this *Journal*, 1952, **29**, 615). The dried gelatine was used for preparing an 1% sol in water; 100 c. c. of this sol were taken in a hysil beaker which had been previously steamed, and the p_H was measured with a hydrogen electrode after successive additions of standard acids or alkalies. These measurements led to the values of N' = amount of acid present in 100 c.c. of the dispersion medium. In another series of measurements pure water instead of the sol was used and these experiments led to the values of p_H against N = amount of acid added per 100 c.c. of the sol. Air was kept out by bubbling hydrogen in the beginning for five minutes. The amount of acid or alkali combined was calculated from the two sets of p_H measurements after applying suitable corrections for the increase in the volume of the mixture. For this purpose Blasel and Matula's formula (*Biochem. Z.*, 1913, **58**, 417, cited and corrected by Hoffman and Gortner, *loc. cit.*) was used,

$$n = N - N' = N - c_H/\alpha,$$

where n = equivalents of acid bound (c_H = conc. of H^+ ions in the equilibrium solution and α = degree of dissociation of the acid). After replacing c_H by c_{OH}, the same equation was also applied for alkalies.

DISCUSSION

Figs. 1 and 2 show the plots of electrolyte bound (n) against equilibrium concentration (N'). One notes that at low concentrations of acids and alkalies the amount of electrolyte bound is practically constant, viz. about 100×10^{-5} g. equivalents per g. gelatine. It is clear from the figures that this quantity cannot be defined with any greater precision. Table I shows that this value is in good agreement with the values usually obtained by previous workers. It appears to us quite reasonable to regard this amount as chemically bound with gelatine, since it corresponds to 'point adsorption' discussed by Gyani in a previous paper (*J. Phys. Chem.*, 1945, **49**, 442) where distinction between adsorption and chemical reaction is lost.

FIG. 1. *Adsorption of acids on gelatine.*

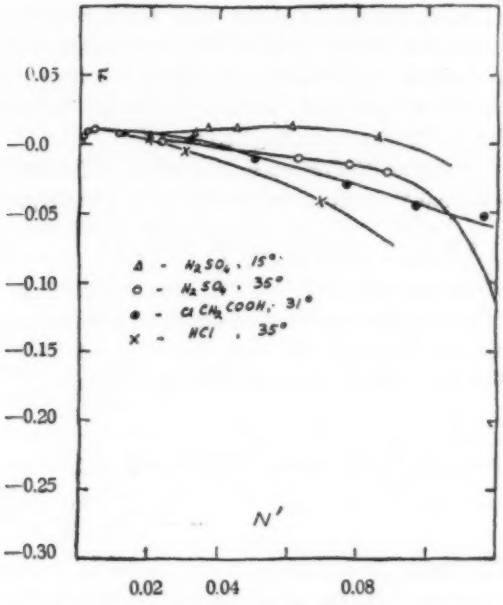
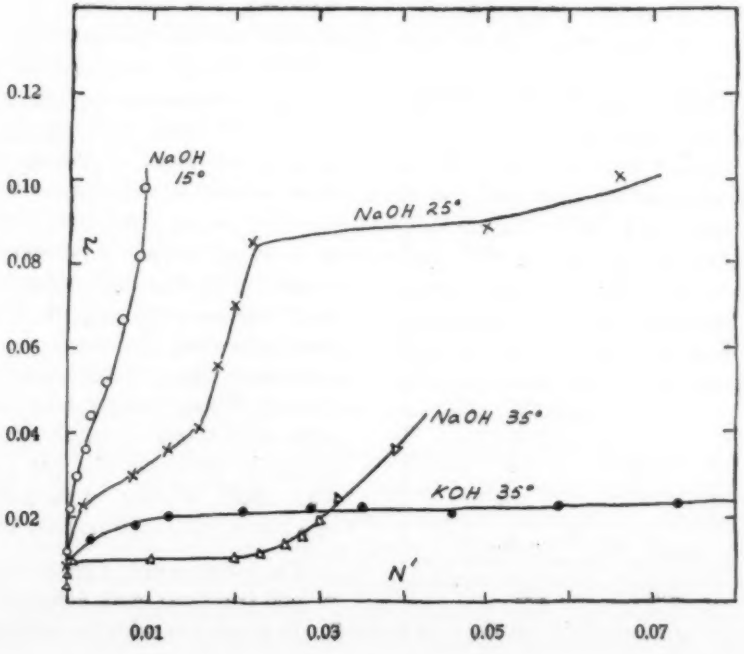


FIG. 2. *Adsorption of alkalies on gelatine.*



The two alkalies show a positive adsorption at all concentrations and at the three temperatures studied (Fig. 2, 15°, 25° and 35°). If the graphs may be regarded as adsorption isotherms, it is curious to note that they change shape remarkably on altering the temperature and the cation. The three isotherms of NaOH, though apparently not similar, may be regarded as belonging to type IV as classified by Brunauer ("Adsorption of Gases and Vapours", Oxford University Press, 1943, p. 150), whereas that for KOH clearly belongs to type I.

The heat of combination of NaOH with gelatine at different stages of combination has been calculated from the isotherms in Fig. 2 using the equation

$$\log\frac{N'_1}{N'_2} = -\frac{Q}{2.303\,R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

where Q = heat of combination, and N'_1 and N'_2 are equilibrium concentrations at temperatures T_1 and T_2, the amount of combination remaining constant. The values so calculated are shown in Table II, and are also plotted in Fig. 3 which shows that one obtains the characteristic W-shaped curve for adsorption.

TABLE II

Heats of combination of NaOH *with gelatine.*

n (equiv. per g. gelatine × 10^5)	0.03	0.04	0.05	0.06	0.07
Q (cal. per equiv. NaOH)	32,614	22,603	19,645	20,800	16,554

One may note that the heats of solution of NaOH or KOH in water (10,350 cal. per g. mol. of NaOH at NaOH : water = 1 : 150 and 13,300 for KOH at KOH : water = 1 : 250) are much smaller. If the combination were a simple neutralisation, one should expect the heat value to be 13,700 ignoring the heats of ionisation. The table above shows that there is a tendency in Q to approach this value as n is increased. It appears to the authors that the high values of Q at small values of n may be related to other structural changes in the gelatine molecule while a simple neutralisation occurs. These changes may be complete when a large number of carboxyl groups in the molecule has combined with alkali, so that in the later stages one gets a value approaching 13,700.

FIG. 3

Isosteric heats of adsorption of NaOH *on gelatine.*

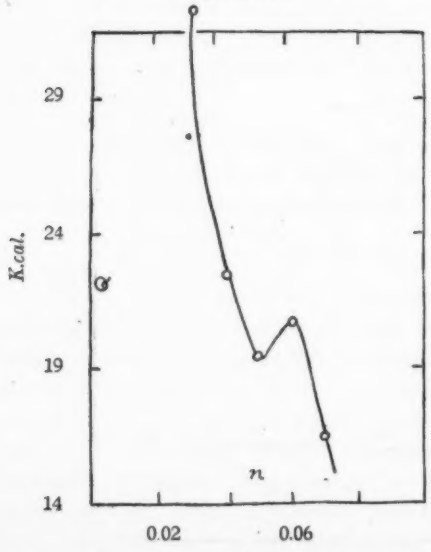


Fig. 1 shows that a positive quantity of acid combines with gelatine only so long as the concentration of the acid is small. If gelatine is added to HCl at 35° so

that the equilibrium concentration of acid (as measured by the concentration of H^+ ions) is more than 0.02*N*, this produces an increase in the concentration of H^+ ions instead of a decrease expected, if there is any combination. This effect is also observed with the other two acids studied, viz., sulphuric and monochloroacetic, though at higher concentrations. This is surprising though negative adsorption has been observed with acetic acid at higher concentrations when the adsorbent is charcoal (Freundlich, "Colloid and Capillary Chemistry", London, 1923, p. 181). This effect is hard to explain since the measurements with hydrogen electrode were quite reproducible and there was no evidence of change of p_H with time. There may not be much point in considering that the electrode might have been poisoned or that there may be progressive hydrolysis. In any case, the general opinion appears to be that hydrolysis, if any, would be small at 35°.

One may consider that gelatine gets hydrated more and more with decrease in p_H. This effect, even if it occurs, must be small, for adsorption measurements of water vapour on gelatine show that the total amount of water does not exceed over 20% of the dry weight of gelatine. Even von Schroeder's paradox (*Z. physikal. Chem.*, 1903, **45**, 75; *Ind. Eng. Chem.*, 1934, **26**, 285) is unlikely to account for this effect.

The dispersion of gelatine in a sol, however, depends on p_H according to Friedman and Klemm (*J. Amer. Chem. Soc.*, 1939, **61**, 1747). They consider that the dispersion increases as the p_H is lowered, *i.e.* in more acid solutions. Combination with acids at different concentrations may therefore be not alike in all details. A rough picture of what happens when acid in sufficient quantity is added to a gelatine sol may be that some of the basic groups are neutralised, and when that happens, some carboxyl groups, which could otherwise have ionised only feebly, may now ionise strongly and thereby increase the concentration of hydrogen ions in solution. Neutralisation of a single basic group may affect several neighbouring carboxyl groups in this manner so that there is a possibility that the concentration of H^+ ions may increase by an amount larger than the acid actually added, and may therefore give the impression of a negative adsorption. This picture implies that there are rather more free carboxyl groups than basic groups. Alternatively, the two may be present in comparable numbers but the dissociation constant of gelatine as an acid may increase greatly on neutralisation of the basic groups. This view would require that the apparent concentration of acid would increase more on the introduction of gelatine if the temperature is higher, which is actually observed.

This latter supposition is somewhat more acceptable. Gelatine on complete hydrolysis gives a number of amino-acids, some of them are monoamino-monocarboxylic and some, diamino-monocarboxylic. In any case, the number of carboxylic groups is never more than that of amino groups (Schmidt, "Text Book of Organic Chemistry", London, 1947, p. 805). Also, one finds that the amounts of acids or alkalies bound at low equilibrium concentrations are comparable in amount, about 100×10^{-5} g. equiv. per g. gelatine. This leads to the supposition that neither

carboxyl nor the basic groups may exist as such but may be in mutually neutralised state. Addition of either acid or base opens up the bonds linking the two.

It appears that while combination of the carboxyl groups by the added alkali progresses, not all the carboxyl groups are easily accessible. The Na^+ ion may diffuse freely to $-COOH$ groups enmeshed within the molecule, but not the larger K^+ ions. Actually it is the OH^- ions derived from either NaOH or KOH which are concerned in neutralisation, but if they were to diffuse alone, the conjugate ions would be outside the molecular mesh and a Donnan equilibrium would ensue, hindering neutralisation. It is possible to understand on this basis why KOH has a differently shaped isosherm in Fig. 2 in contrast to that for NaOH, and why the combining alkali is so restricted in amount even at saturation (shown by the almost horizontal portion of the isotherm).

Further work is in progress. One of us (J. C. G.) thanks the Patna University for the grant of a research scholarship.

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OXALENEDIAMIDOXIME. PART III. ESTIMATION OF PALLADIUM

By P. R. Dasgupta

Oxalenediamidoxime has been used for the estimation of palladium up to 0.001 g. and for its separation from moderate amounts of nickel and platinum at a p_H range of 4-6.

Oxalenediamidoxime has been used successfully for the estimation of nickel and its separation from cobalt, zinc and manganese (Chatterjee, this *Journal*, 1938, 15, 608) and from chromium and aluminium (Kuras, *Trav. Chim. Tchecoslov.*, 1947, 12, 198).

It has been found by the author that palladium is quantitatively precipitated as the palladium complex of oxalenediamidoxime, without interference from other metallic ions, such as nickel and platinum, and in presence of either a mixture of ammonium chloride and ammonia or a mixture of hydroxylamine hydrochloride and ammonia. Oxalenediamidoxime is water-soluble and has an obvious advantage over other reagents which are made up in organic solvents.

Experimental

In the preparation of oxalenediamidoxime Fischer's method (cf. Chatterjee, *loc. cit.*) was followed; an 1% solution of the reagent was used in all the estimations.

Palladium Oxalenediamidoxime.—The light yellow crystalline precipitate of the palladium complex was obtained by mixing solutions of palladous chloride (1 mol.) and oxalenediamidoxime (2 mols.) in the presence of ammonium chloride and ammonium hydroxide.

The complex (m.p. 270°, decomp.) contains two molecules of water of crystallisation, one of which is removed on heating to 100° and the remaining one on further heating to 110°. [Found : H_2O (in an air-dried crystalline sample), 9.02. Pd. $(C_2H_5O_2N_4)_2$, 2 H_2O requires H_2O, 9.5 per cent (in a desiccated sample). Found : Pd, 31.0. Calc. Pd, 31.3 per cent]. It is insoluble in water and in almost all other organic solvents such as ethanol, methanol, acetone, benzene, chloroform, etc. It is soluble in warm dilute hydrochloric acid ; the solution deposits pale yellow glistening needles on cooling. The crystals give positive test for chloride ion, their m.p. being 225° with decomposition.

Estimation of Palladium in presence of Ammonium Chloride and Ammonia.—A solution of palladium chloride was reduced with sodium formate and the precipitated metallic palladium was thoroughly washed and dissolved again in boiling conc. HCl containing a small quantity of conc. HNO_3. A transparent, dark brown coloured solution was obtained which was evaporated twice to dryness in the presence of conc. HCl. The solid residue of palladium dichloride was dissolved in boiling water containing a small quantity of conc. HCl. The brown solution was filtered twice and the filtrate contained about 0.2 g. of palladium in 100 c.c. of the solution. Certified standard pipettes were used in all measurements.

Palladium chloride solution (10 c.c.) was mixed with a dilute solution of ammonium hydroxide until the orange coloured flocculent precipitate which appeared at first redissolved, forming a colorless transparent solution. The reagent (15 c.c.) was added to this faintly ammoniacal solution (0.75 g. of oxalenediamidoxime for 1 g. of palladium). The colour of the solution changed quickly to light yellow and within 3 to 5 minutes pale yellow, crystalline needles of the palladium complex appeared. The mixture was left overnight, filtered through asbestos Gooch crucible and the precipitate was washed free of chloride with cold ammoniacal water, dried at 100°-115° and then weighed as anhydrous dioxime.

Table I shows a comparison of the results obtained by the new reagent with those obtained by the dimethylglyoxime and reduction methods. It will be observed that the results obtained by the oxalenediamidoxime agree more closely with those obtained by the reduction method. The p_H values of the undiluted filtrate, collected initially after the separation of the palladium complex, were determined potentiometrically.

TABLE I

p_H of the medium.	Wt. of $Pd(C_2H_5O_2N_4)_2$.	Corresponding wt. of Pd.	Wt. of Pd as estimated by Demethylglyoxime.	Reduction.
7.4	0.08622 g.	0.02699 g.	0.02690 g.	0.02701 g.
8.0	0.08624	0.02700	0.02686	0.02725
7.8	0.05630	0.01763	0.01760	0.01765
7.6	0.01110	0.03475	0.03460	0.03471

Estimation of Palladium in presence of Hydroxylamine Hydrochloride and Ammonium Hydroxide.—To a standard solution of palladium chloride (10 c.c.) was added hydroxylamine hydrochloride (0.5 to 1 g.). The solution was then treated with dilute ammonium hydroxide until its brown colour just disappeared. The reagent solution (15 c.c.) was then added when a very pale yellow precipitate of the palladium complex appeared within 2 to 3 minutes. The precipitate was left overnight, filtered through an asbestos Gooch crucible, washed free of chloride ion with 50 c.c. of cold ammoniacal water, dried at 110°-115°, cooled and weighed.

The p_H values of the undiluted filtrates were determined potentiometrically. Results of three different determinations are shown in Table II.

TABLE II

p_H of the medium.	Wt. of $Pd(C_2H_5O_2N_4)_2$.	Corresponding wt. of Pd.	Wt. of Pd present.	Error.
6.2	0.0723 g.	0.02263 g.	0.02263 g.	Nil
6.8	0.0725	0.02270	0.02263	+0.00007
6.0	0.0721	0.02257	0.02263	−0.00006

The smallest amount of palladium that has been estimated with a fair degree of accuracy by the use of oxalenediamidoxime is shown in Table III. The solution of palladium chloride employed for this experiment contained 0.00088 g. of palladium per c.c. of the solution. Aliquots of this solution were estimated with the reagent.

TABLE III

Wt. of Pd found.	Wt. of Pd present.	Error.
0.010550 g.	0.010560 g.	−0.00001 (0.095%)
0.005276	0.005280	−0.000004 (0.076%)
0.002640	0.002640	Nil (0.000%)
0.002104	0.002112	−0.000008 (0.379%)
0.001754	0.001758	−0.000004 (0.228%)
0.001049	0.001056	−0.000007 (0.663%)

Separation of Palladium from Nickel.—Mixtures containing 10 c.c. of a solution of palladium chloride containing 0.0226 g. of palladium metal, and different volumes of a standard solution of nickel chloride, containing 0.0496 g. of metallic nickel in 10 c.c. of the solution, were treated with a very dilute solution of ammonium hydroxide until the orange flocculent precipitate (due to palladium) which appeared at first just redissolved into a clear solution of bluish violet colour (due to nickel); 5 c.c. of acetic acid-sodium acetate buffer (p_H 4-6) were added, followed by 20 c.c. of the reagent. The colour of the solution became violet finally and a light yellow precipitate started appearing after 5 to 8 minutes. On standing overnight, it was filtered, washed with a buffer solution first and then with 100 c.c. of cold ammoniacal water (2-4% approx.), dried at 110°-115° and weighed as $Pd(C_2H_5O_2N_4)_2$. The results are shown in Table IV.

TABLE IV

Composition of the mix.	Pd found.	Diff.	Error.
Pd : 0.02260 g. Ni : 0.00496	0.02254 g.	−0.00006 g.	−0.2%
Pd : 0.02260 Ni : 0.00992	0.02257	−0.00003	−0.1%
Pd : 0.02260 Ni : 0.01488	0.02284	+0.00024	+0.8%
Pd : 0.02260 Ni : 0.01984	0.02355	+0.00095	+4.0%
Pd : 0.02260 Ni : 0.02480	0.03475	+0.01215	
Pd : 0.02260 Ni : 0.02970	0.02536	+0.00276	
Pd : 0.02260 Ni : 0.03470	0.02880	+0.00620	

The estimation of palladium from a mixture of palladium and nickel seems to be accurate only when the proportion of nickel : palladium as metals present in the mixture is about 1 : 2 by weight.

Separation of Palladium from Platinum.—Mixtures containing a solution having 0.0226 g. of palladium and different amounts of platinum, respectively, were treated with about an equivalent quantity (with respect to platinum) of hydroxylamine hydrochloride crystals, followed by a dilute solution of ammonia until a clear and colorless solution was obtained. The solution was still acidic to litmus ; 20 c.c. of the reagent were then added to the mixture to obtain a pale yellow precipitate of the palladium complex which was allowed to settle overnight, then washed carefully with 50 c.c. of cold ammoniacal water, dried at 110°-115° and finally weighed as $Pd(C_2H_5O_2N_4)_2$.

The p_H of the undiluted filtrates obtained after separation of the precipitate was determined potentiometrically. Table V shows the results.

TABLE V

p_H of the medium.	Composition of the mix.	Pd found.	Diff.	Error.
5.6	Pd : 0.02260 g. Pt : 0.00416	0.02270 g.	+0.00010	+0.5%
6.2	Pd : 0.02260 Pt : 0.00832	0.02267	+0.00007	+0.3%
6.0	Pd : 0.02260 Pt : 0.01248	0.02273	+0.00013	+0.5%
5.7	Pd : 0.02260 Pt : 0.01664	0.02427	+0.00167	+8.0%
5.8	Pd : 0.02260 Pt : 0.02080	0.02662	+0.00402	
6.0	Pd : 0.02260 Pt : 0.02496	0.02724	+0.00464	

The estimation of palladium in the presence of platinum is found to be successful only when the proportion of platinum : palladium as metals in the mixture is about 1 : 2 by weight.

The author is indebted to Dr. Ramgopal Chatterjee for his unstinted help and constant guidance throughout the course of the work and Professor P. C. Rakshit, Head of the Dept. of Chemistry, for laboratory facilities.

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PECHMANN CONDENSATION. PART II. CONDENSATION OF 2:5-DIALKYLPHENOLS WITH β-KETONIC ESTERS

By R. N. Usgaonkar, V. M. Thakor, G. V. Jadhav and R. C. Shah

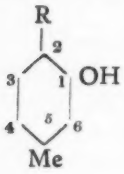
2-Ethyl-5-methylphenol on Pechmann condensation with ethyl acetoacetate in presence of sulphuric acid or aluminium chloride (nitrobenzene) gave 4 : 7-dimethylcoumarin, the ethyl group being eliminated. The same compound was obtained when thymol was similarly condensed in presence of aluminium chloride. In presence of phosphorus pentoxide, however, the usual condensation occurred and the corresponding chromone derivatives were isolated. The two phenols condensed with ethyl α-methylacetoacetate in presence of phosphorus oxychloride or phosphorus pentoxide to give the corresponding chromone derivatives. 2-Ethyl-4-bromo-5-methylphenol and 4-bromothymol when condensed with ethyl acetoacetate in presence of sulphuric acid furnished chromone derivatives.

Recently Mody and Shah (*Proc. Ind. Acad. Sci.*, 1951. **34A**, 77) observed that methyl α-resorcylate on Pechmann condensation with ethyl acetoacetate in presence of concentrated sulphuric acid gave a mixture of 7-hydroxy-2-methyl-5-carbomethoxychromone and 5-hydroxy-4-methyl-7-carbomethoxycoumarin. Its condensation with malic acid, however, furnished only a 7-hydroxycoumarin derivative.

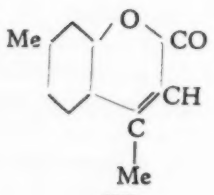
It was thought of interest to further investigate this behaviour and a systematic study was therefore undertaken in this laboratory, and the Pechmann condensation of several 2 : 5-dialkyl-substituted phenols was carried out.

2-Ethyl-5-methylphenol (I, R=Et) on condensation with ethyl acetoacetate in presence of 80% sulphuric acid or anhydrous aluminium chloride (nitrobenzene) furnished a product which was identified as **4** : 7-dimethylcoumarin (II), thus showing that the ethyl group was eliminated and the ring-closure occurred at that position. The same coumarin was obtained when thymol (I, R=*iso*Pr) was condensed with ethyl acetoacetate in presence of anhydrous aluminium chloride, the *iso*propyl group being removed. However, in presence of phosphorus pentoxide in case of both the phenols, the condensation occurred in the 6-position and 2 : 5-*dimethyl*-8-*ethylchromone* (III, R_1 = Et, R_2 = H) and 2 : 5-*dimethyl*-8-iso*propylchromone* (III, R_1 = *iso*Pr, R_2 = H) respectively were obtained. In both the cases, by-products were obtained which did not appear to be either coumarins or chromones as they did not give a methoxycinnamic acid or a styryl derivative. Goodall and Robertson (*J. Chem. Soc.*, 1936, 426) have isolated a similar product during the condensation of *p*-xylenol and ethyl α-benzylacetoacetate. The condensation of 2-benzyl-5-methylphenol (I, R = CH_2Ph) with ethyl acetoacetate in presence of

phosphorus pentoxide gave 2 : 5-dimethyl-8-benzylchromone (III, $R_1 = CH_2Ph$, $R_2 = H$).



(I)



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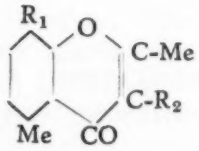

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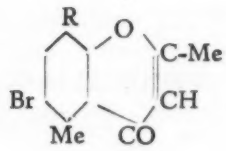

(IV)

The present observation of elimination of alkyl groups is interesting as these are the first instances where elimination during the Pechmann condensation has been observed ; though elimination of such groups in presence of concentrated sulphuric acid (cf. "Organic Reactions", Vol. I, p. 371, J. Willey and Sons) or anhydrous aluminium chloride (cf. Thomas, "Anhydrous Aluminium Chloride in Organic Chemistry") is known.

2-Ethyl-5-methylphenol (I, R = Et) and thymol (I, R = *iso*Pr) condensed with ethyl α-methylacetoacetate in presence of phosphorus oxychloride or phosphorus pentoxide to give 8-ethyl-(III, $R_1 = Et$, $R_2 = Me$) and 8-*iso*propyl-2 : 3 : 5-trimethylchromones (III, $R_1 = iso$Pr, $R_2 = Me$) respectively. Similar observation of formation of chromone using phosphorus oxychloride has been made by Goodall and Robertson (*loc. cit.*) in case of 2 : 5-xylenol.

2-Ethyl-4-bromo-5-methylphenol and 4-bromothymol condensed with ethyl acetoacetate in presence of concentrated sulphuric acid and phosphorus pentoxide to furnish 8-ethyl- and 8-*iso*propyl-2 : 5-dimethyl-6-bromochromones (IV, R = Et and *iso*Pr) respectively, as both gave styryl derivatives. These are two more instances where during Pechmann condensation in presence of sulphuric acid chromone formation is found to occur. This is interesting, as generally in presence of this reagent coumarins are formed and there are only three known instances where chromone formation is observed using this reagent (cf. Mody and Shah, *loc. cit.*).

EXPERIMENTAL

2-Ethyl-5-methylphenol (I, R = Et) was prepared by the Clemmensen reduction of 2-acetyl-5-methylphenol (40 g.) with zinc amalgam (from 100 g. zinc dust and 10 g. mercuric chloride in 200 c. c. water) and hydrochloric acid (1 : 1, 200 c. c.) for 6 to 7 hours on a steam-bath. 2-Ethyl-5-methylphenol, which separated as an oil, solidified on cooling (m.p. 41-43°) and was collected, washed and crystallised from petroleum ether in colorless rhombic crystals, m.p. 43-44°. Auwers, Bundesman and Wieners (*Annalen*, 1925, 447, 78) give the same m.p.

Pechmann Condensation of 2-*Ethyl*-5-*methylphenol* (I, R = Et) *with Ethyl Acetoacetate*: 4 : 7-*Dimethylcoumarin* (II)

1. *In presence of* 80% *Sulphuric Acid.*—2-Ethyl-5-methylphenol (20.0 g.) and ethyl acetoacetate (19.0 g.) were mixed and sulphuric acid (80%, 130 c. c.) was slowly added with shaking. It was kept for 48 hours, poured over crushed ice and extracted with ether. The extract was washed several times with sodium hydroxide solution (2%), then with water, dried and the ether removed. The oil that remained deposited some crystals which were collected and crystallised from alcohol (95%) in colorless needles, found to be 4 : 7-dimethylcoumarin (II), m.p. and mixed m. p. 130-31° (< 0.1 g.). Fries and Klestermann (*Ber.*, 1906, **39**, 871) give m. p. 131-32°.

2. *In presence of Anhydrous Aluminium Chloride.*—To 2-ethyl-5-methylphenol (15.0 g.) and ethyl acetoacetate (14.0 g.) in nitrobenzene (16 c. c.) at 100° (oil-bath) was gradually added anhydrous aluminium chloride (28.0 g.) in nitrobenzene (100 c. c.) with mechanical stirring within a period of an hour. The temperature of the bath was then raised to 120°-125° and maintained for 3 hours. It was cooled, ice and hydrochloric acid added, and steam passed to remove nitrobenzene. The uncrystallisable black pasty mass was subjected to distillation under reduced pressure (15 mm.). The distillate (*c.* 3.0 g.) on crystallisation from ethanol gave a product, m.p. 120-30° (*c.* 1.0 g.) which on further crystallisation from the same solvent gave 4 : 7-dimethylcoumarin, m.p. and mixed m.p. 131-32° (yield 0.1 g.). No other pure product could be isolated. Further work is in progress.

No definite product could be isolated when the condensation was carried out in presence of phosphorus pentoxide.

Condensation of 2-*Ethyl*-5-*methylphenol* (I, R = Et) *with Ethyl Acetoacetate in presence of Phosphorus Pentoxide*: 2 : 5-*Dimethyl*-8-*ethylchromone* (III, R_1 = Et, R_2 = H) *and a product of m.p.* 108°

A mixture of the phenol (10.0 g.) and ethyl acetoacetate (10.0 g.) was heated with phosphorus pentoxide (15.0 g.) for an hour on a steam-bath, some more oxide (15.0 g.) was added and heating continued for 2 hours. It was digested with water, basified with dilute sodium hydroxide solution and extracted with ether. The extract was washed several times with 2% sodium hydroxide solution and then with water, dried and the ether removed. The oil that remained, on treatment with petroleum ether, on cooling at (0°) gave a solid product which crystallised from alcohol in yellowish plates, m.p. 108°. (Found : C, 71.3 ; H, 6.0%). It did not give a methoxycinnamic acid derivative nor a styryl derivative. It could not be precipitated from its alcoholic solution by addition of dilute sodium hydroxide solution. The petroleum ether solution on concentration and cooling gave 2 : 5-*dimethyl*-8-*ethylchromone* (III, R_1 = Et, R_2 = H) which crystallised from the same solvent in colorless needles, m.p. 62-64°. (Found : C, 76.7 ; H, 6.6. $C_{13}H_{14}O_2$ requires C, 77.2 ; H, 6.9 per cent). It is insoluble in water, soluble in petroleum ether, easily

soluble in alcohol, acetone, ether and acetic acid. It can be reprecipitated from its alcoholic solution by adding 10% sodium hydroxide solution.

The chromone (0.50 g.) and piperonal (0.35 g.) in absolute alcohol (10 c. c.) with metallic sodium (0.06 g.), when heated on a steam-bath for 2 hours, gave 2-(3' : 4'-*methylenedioxystyryl*)-5-*methyl*-8-*ethylchromone* which separated as a yellow solid on cooling and was crystallised from alcohol in tiny plates, m.p. 172-73°. (Found : C, 75. 4 ; H, 5.7. $C_{21}H_{18}O_4$ requires C, 75.4 ; H, 5.4 per cent).

Condensation of 2-*Ethyl*-5-*methylphenol* (I, R = Et) *with Ethyl* α-*Methylacetoacetate* : 2 : 3 : 5-*Trimethyl*-8-*ethylchromone* (III, R_1 = Et, R_2 = Me)

1. *In presence of Phosphorus Pentoxide.*—A mixture of the phenol (10.0 g.), ethyl α-methylacetoacetate (10.0 g.) and phosphorus pentoxide (15.0 g.) was heated on a steam-bath for an hour, more oxide (15.0 g.) added and heating continued for further 2 hours. It was worked up as in the previous case and the semi-solid mass that remained on removal of ether, was crystallised from alcohol (95%) when 2 : 3 : 5 -*trimethyl*-8-*ethylchromone* (III, R_1 = Et, R_2 = Me) separated in colorless plates, m.p. 88-89°. (Found : C, 77.3 ; H, 7.0. $C_{14}H_{16}O_2$ requires C, 77.7 ; H, 7.4 per cent). It is sparingly soluble in petroleum ether, easily soluble in alcohol, acetone and acetic acid.

2. *In presence of Phosphorus Oxychloride.*—The phenol (10.0 g.), ethyl α-methylacetoacetate (10.0 g.) and phosphorus oxychloride (5.0 c. c.) were heated on a steam-bath for 3 hours, treated with water and the whole mass extracted with ether after cooling. The extract after working up as usual gave the same chromone, m.p. and mixed m.p. 88-89°.

No definite product was obtained when sulphuric acid was used as a condensing agent.

The styryl derivative, 2-(3' : 4'-*methylenedioxystyryl*)-3 : 5-*dimethyl*-8-*ethylchromone*, obtained as before, was crystallised from absolute alcohol in tiny yellow needles, m.p. 181-82°. (Found : C, 75.9 ; H, 5.9. $C_{22}H_{20}O_4$ requires C, 75.9 ; H, 5.7 per cent).

2-*Ethyl*-4-*bromo*-5-*methylphenol.*—2-Ethyl-5-methylphenol (10.0 g.) in acetic acid (10 c.c.) was treated with bromine in acetic acid (20%, 60 c.c.) at 0° and kept at that temperature for half an hour. It was diluted with water and the bromophenol separating was collected, washed and crystallised from dilute acetic acid in long colorless needles, m.p. 89-90° (shrinks at 80°). (Found : C, 49.6 ; H, 4.8. $C_9H_{11}OBr$ requires C, 50.2 ; H, 5.1 per cent).

Condensation of 2-*Ethyl*-4-*bromo*-5-*methylphenol with Ethyl Acetoacetate* : 2 : 5-*Dimethyl*-6-*bromo*-8-*ethylchromone* (IV, R = Et)

1. *In presence of Sulphuric Acid.*—A mixture of the bromophenol (3.0 g.), ethyl acetoacetate (2.2 g.) and concentrated sulphuric acid (20 c.c.) was heated on a steam-bath for 5-10 minutes and kept for 20 hours. It was worked up as usual, the solid

obtained was collected, washed and crystallised from alcohol (95%) when 2 : 5-*dimethyl*-6-*bromo*-8-*ethylchromone* (IV, R = Et) separated in colorless needles, m.p. 127-28°. (Found : C, 54.9 ; H, 4.32. $C_{13}H_{13}O_2Br$ requires C, 55.4 ; H, 4.6 per cent).

2. *In presence of Phosphorus Pentoxide.*—The bromophenol (3.0 g.), ethyl acetoacetate (2.2 g.) and phosphorus pentoxide (5.0 g. + 5.0 g.) were heated for 3 hours on a steam-bath. It was worked up as usual, when the above chromone, m.p. and mixed m.p. 127-28°, was obtained.

When the condensation was attempted in presence of phosphorus oxychloride or anhydrous aluminium chloride (nitrobenzene), only blackish unworkable products were obtained.

With piperonal, the bromochromone gave 2-(3' : 4'-*methylenedioxystyryl*)-5-*methyl*-6-*bromo*-8-*ethylchromone* which was crystallised from glacial acetic acid in tiny yellow needles, m.p. 230-31°. (Found : C, 60.5 ; H, 4.0. $C_{21}H_{17}O_4Br$ requires C, 61.0 ; H, 4.1 per cent).

Condensation of 2-iso*Propyl*-5-*methylphenol* (*Thymol*) (I, R = isoPr) *with Ethyl Acetoacetate in presence of Anhydrous Aluminium Chloride*

4 : 7-*Dimethylcoumarin* (II).—Thymol (20.0 g.) and ethyl acetoacetate (19.0 g.) in dry nitrobenzene (20 c.c.) at 100° were treated with anhydrous aluminium chloride (36.0 g.) in nitrobenzene (120 c.c.) and the reaction mixture was then heated at 120°-125° for 2 to 3 hours and worked up as in the previous case. The blackish residue was subjected to distillation under reduced pressure and the yellow distillate on working up furnished 4 : 7-dimethylcoumarin (II), crystallised from alcohol (95%), m.p. and mixed m.p. 131-32°.

When the condensation was carried out in presence of sulphuric acid or phosphorus oxychloride, no pure product could be isolated.

Condensation of 2-iso*Propyl*-5-*methylphenol* (*Thymol*) (I, R = isoPr) *with Ethyl Acetoacetate in presence of Phosphorus Pentoxide*

2 : 5-*Dimethyl*-8-iso*propylchromone* (III, R_1 = iso Pr, R_2 = H) *and a product of m.p.* 123-25°.—Thymol (10.0 g.), ethyl acetoacetate (9.0 g.) and phosphorus pentoxide (15.0 g.) were heated on a steam-bath for an hour, additional oxide (15.0 g.) added and the mixture further heated for 2 hours and worked up as before. The dark thick oil obtained on removal of the ether was treated with petroleum ether. On cooling (0°) a solid product was obtained which was collected, washed with petroleum ether and crystallised from alcohol in clusters of needles, m.p. 123-25°. (Found : C, 72.23 ; H, 6.86%). It cannot be precipitated from alcoholic solution by adding dilute sodium hydroxide solution. It did not give a methoxycinnamic acid, nor a styryl derivative.

The product, soluble in petroleum ether, on removal of the solvent gave an oil, which was distilled under reduced pressure (165°-180°/5 mm.) when 2 : 5-*dimethyl*-8-iso*propylchromone* (III, R_1 = *iso*Pr, R_2 = H) came over as a yellow oil which soon solidified. It crystallised from petroleum ether in colorless flat needles, m.p. 63-64°.

(Found : C, 77.6 ; H, 7.7. $C_{14}H_{16}O_2$ requires C, 77.8 ; H, 7.5 per cent). It is insoluble in dilute sodium hydroxide solution and can be reprecipitated from its alcoholic solution by addition of cold dilute sodium hydroxide solution.

2-(3′ : 4′-*Methylenedioxystyryl*)-5-*methyl*-8-iso*propylchromone* was obtained from the above chromone and piperonal and crystallised from absolute alcohol in long yellow needles, m.p. 189-90° (shrinks at 180°). (Found : C, 76.2 ; H, 5.6. $C_{22}H_{20}O_4$ requires C, 75.9 ; H, 5.7 per cent).

Condensation of 2-iso*propyl*-5-*methylphenol* (*Thymol*) (I, R = isoPr) *with Ethyl* α-*Methylacetoacetate* : 2 : 3 : 5-*Trimethyl*-8-iso*propyl-chromone* (III, R_1 = isoPr, R = Me)

1. *In presence of Phosphorus Pentoxide.*—Thymol (10.0 g.), ethyl α-methyl-acetoacetate (10.0 g.) and phosphorus pentoxide (15.0 g.+15.0 g.) were heated on a steam-bath for 3 hours. Water was added and the product worked up as usual when 2 : 3 : 5-*trimethyl*-8-iso*propylchromone* (III, R_1 = *iso*Pr, R_2 = Me) separated from rectified spirit in colorless needles, m.p. 98-99°. (Found : C, 78.0 ; H, 7.5. $C_{15}H_{18}O_2$ requires C, 78.3 ; H, 7.8 per cent). It is sparingly soluble in petroleum ether and soluble in alcohol, acetic acid, acetone and ether.

2. *In presence of Phosphorus Oxychloride.*—When the condensation of thymol (10.0 g.) with ethyl α-methylacetoacetate (10.0 g.) was carried out in the presence of phosphorus oxychloride (5 c. c.) on a steam-bath (2-3 hours), and the reaction mixture worked up as usual, the same chromone, m.p. and mixed m.p. 98-99°, was obtained.

2-(3′ : 4′-*Methylenedioxystyryl*)-3 : 5-*dimethyl*-8-iso*propylchromone* was obtained from the above chromone and piperonal and was crystallised from alcohol in yellow needles, m.p. 174-75°. (Found : C, 76.0 ; H, 5.8. $C_{23}H_{22}O_4$ requires C, 76.2 ; H, 6.1 per cent).

Condensation of 2-iso*Propyl*-4-*bromo*-5-*methylphenol* (4-*Bromothymol*) *with Ethyl Acetoacetate* : 2 : 5-*Dimethyl*-6-*bromo*-8-iso*propyl-chromone* (IV, R = isoPr)

1. *In presence of Sulphuric Acid.*—A mixture of 4-bromothymol (8.0 g.), ethyl acetoacetate (5.0 g.) and concentrated sulphuric acid (60 c. c.) was warmed on a steam-bath for 5-10 minutes and then left at room temperature (*c.* 30°) for 20 hours. It was treated with water and worked up as usual. 2 : 5-*Dimethyl*-6-*bromo*-8-iso*propylchromone* (IV, R = *iso*Pr) obtained was crystallised from rectified spirit in colorless rods, m.p. 114-15°. (Found : C, 56.9 ; H, 4.9. $C_{14}H_{15}O_4Br$ requires C, 56.9 ; H, 5.1 per cent).

2. *In presence of Phosphorus Pentoxide.*—4-Bromothymol (8.0 g.), ethyl acetoacetate (5.0 g.) and phosphorus pentoxide (15.0 g.+15.0 g.) were heated on a steam-bath for 3 hours. It was digested with water and worked up as usual when the above chromone, m.p. and mixed m.p. 114-15°, was obtained.

When the condensation was attempted using phosphorus oxychloride or anhydrous aluminium chloride (nitrobenzene), only pasty unworkable products were isolated.

2-(3′ : 4′-*Methylenedioxystyryl*)-5-*methyl*-6-*bromo*-8-iso*propylodromone*, obtained from the above chromone and piperonal, was crystallised from acetic acid in yellow cubes, m.p. 274-75°. (Found : C, 61.5 ; H, 4.5. $C_{22}H_{19}O_4Br$ requires C, 61.8 ; H, 4.5 per cent).

2-*Benzyl*-5-*methylphenol* (I, R = CH_2Ph) was prepared by the Clemmensen reduction of 2-benzyl-5-methylphenol (40 g.) with zinc amalgam (from 100 g. of zinc dust) and concentrated hydrochloric acid (1 : 1, 700 c. c) on a steam-bath for 6 to 7 hours. The oil that separated on cooling was taken up in ether, which was dried and the ether removed. It was distilled under reduced pressure (179-180°/5 mm.) and the colorless oil obtained soon solidified, m.p. 46-47° (25-30 g.). Huston and Houk (*J. Amer. Chem. Soc.*, 1932, **54**, 1507) give the same melting point.

Condensation of 2-*Benzyl*-5-*methylphenol* (I, R = CH_2PH) *with Ethyl Acetoacetate in presence of Phosphorus Pentoxide*

2:5-*Dimethyl*-8-*benzylchromone* (III, $R_1 = CH_2PH$, $R_2 = H$).—The phenol (10 g.), ethyl acetoacetate (7.0 g.) and phosphorus pentoxide (15.0 g.+15.0 g.) were heated on a steam-bath for 3 hours. Water was added and the reaction mixture worked up as usual. The *chromone* (III, $R_1 = CH_2Ph$, $R_2 = H$) obtained was crystallised from dilute alcohol in clusters of needles, m.p. 89-90°. (Found : C, 81.2 ; H, 6.1. $C_{18}H_{16}O_2$ requires C, 81.3 ; H, 6.1 per cent).

The condensation of this phenol in presence of sulphuric acid or anhydrous aluminium chloride (nitrobenzene) did not furnish any product.

2-(3′ : 4′-*Methylenedioxystyryl*)-5-*methyl*-8-*benzylchromone*, preparad as usual from the above chromone and piperonal, was crystallised from a mixture of alcohol and acetic acid in yellow needles, m.p. 219-20°. (Found : C, 78.5 ; H, 5.4. $C_{26}H_{20}O_4$ requires C, 78.8 : H, 5.1 per cent).

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ELECTROMETRIC STUDIES OF RATE OF ADSORPTION OF ACIDS BY SUGAR CHARCOAL FROM AQUEOUS SOLUTIONS

By Kesho Dass Jain

The rate of adsorption of formic, acetic, benzoic, oxalic, malonic, succinic, citric and phosphoric acids on activated sugar charcoal has been studied potentiometrically using quinhydrone electrode.

In all cases, equilibrium is reached in 20 to 60 minutes. The reaction is reversible and takes time to attain equilibrium. The rate of adsorption is found to increase with increasing amounts of charcoal. The time for saturation is not affected by increasing the amounts of charcoal.

Velocity constants of adsorption, calculated on the assumption of monomolecular reaction, show that adsorption consists of two consecutive processes, the first, rapid, going on for a few minutes, and the second, slower, giving nearly constant values for velocity constant for monomolecular reaction.

Small time for saturation and rapid process of adsorption suggest that complications are liable to occur on the surface of the adsorbent.

The rate at which adsorption equilibrium is established is an important factor in many physical, chemical and biological phenomena. The time required to attain equilibrium has been found by many to range from a few seconds up to several hours, depending on the nature of the process taking place.

The adsorption from solutions by solid adsorbents is characterised by high adsorption velocities. Marc (*Z. Elektrochem.*, 1914, **20**, 515), Arendt (*Koll.-Chem. Beih.*, 1905, **7**, 212), Swearingen and Dickonson (*J. Phys. Chem.*, 1932, **36**, 534) have shown that equilibrium is reached rapidly in many cases, and in some cases the rate is very slow. The time required for equilibrium to be reached ranges from several minutes to several hours. Angelesen and Seoloviu (*Bull. Soc. Chem. Romania*, 1938, **20**, 197) found adsorption of acetic acid and oxalic acid on active charcoal to consist of two consecutive processes, the first, rapid and the second, slower, conforming to the equation for unimolecular reaction. The velocity of the initial process increases with the concentration and with the capillary activity of the solute.

While studying the adsorption of mono- and polybasic acids, bi-salts and hydroxybenzenes by sugar charcoal, Jain and Jha (this *Journal*, 1940, **17**, 685; 1941, **18**, 321, 585) found no deviation from the general laws in case of monobasic acids and monohydroxybenzenes, but polybasic acids, bi-salts and dihydroxybenzenes gave adsorption curves of zigzag and periodic type. In order to find out some explanation for this behaviour of these substances on the surface of sugar charcoal (used in the previous work), electrometric study of the rate of adsorption of acids by sugar charcoal was undertaken. Small time for saturation and a rapid process of adsorption suggested the complexity occurring on the surface of the adsorbent.

Experimental

The apparatus used for determining the rate of adsorption of acids by sugar charcoal consisted of a potentiometric arrangement.

Procedure.—The hydrogen-ion concentration or p_H of acid solutions was measured with the help of the quinhydrone electrode in conjunction with a normal

calomel electrode, at various intervals of time. In a small, clean and dry beaker, a measured volume of the solution of acids of known strength was taken. Quinhydrone was dropped in and was shaken well, and the E. M. F. was measured. Then a weighed quantity of sugar charcoal was put into the solution which was well agitated from time to time. The stop-watch was started just when the charcoal was added, and agitated. When there was no deflection of the spot of light on either side of the scale, the E.M.F.'s were noted. The p_H of the solution was calculated, and then the velocity constant of adsorption of different acids was calculated on the basis of unimolecular reaction. The results for different acids are shown in Table I.

TABLE I

Rate of adsorption of acids by charcoal.

Charcoal taken – 0.5 g. 0.2 *N*-acid soln. taken – 50 c.c. Temp. – 30°.

Time.	p_H.	$1/H^+$.	k.	Time.	p_H.	$1/H^+$.	k.	Time.	p_H.	$1/H^+$.	k.
	Oxalic acid.				Malonic acid.				Succinic acid.		
0 min.	4.053	11310		0 min.	4.334	21820		0 min.	4.564	36670	
7	4.106	12770		2	4.357	22750		5	4.624	42090	
10	4.116	12770		4	4.375	23710		10	4.628	42440	0.00066
16	4.115	13020	0.00140	6	4.386	24310		15	4.635	43160	0.000108
20	4.122	13240	0.00157	8	4.388	24430	0.00105	18	4.639	43590	0.00.07
25	4.132	13560	0.00173	13	4.396	24920	0.0015	25	4.645	44170	0.00104
28	4.138	13740	0.00175	15	4.399	25050	0.0015	32	4.650	44700	0.00104
33	4.144	13920	0.00183	17	4.400	25190	0.0014	35	...	...	...
35	...	...	...	20	4.404	25260	0.0013	40	...	...	...
40	...	...	...	25	...	...	...				
	Phosphoric acid.				Benzoic acid.				Acetic acid.		
0 min.	4.163	14630		0 min.	4.776	59700		0 min.	4.671	46900	
5	4.285	19269		2	4.779	60200	0.0018	5	4.702	50390	
7	4.294	19780	0.058	10	4.794	52230	0.0018	8	4.714	51760	0.0038
10	4.314	20620	0.00598	15	4.800	63060	0.0016	10	4.722	52700	0.0038
16	4.350	22390	0.00594	20	4.803	63490	0.0013	14	4.736	54480	0.0037
20	4.371	23530	0.0058	25	...	...	...	19	4.754	56700	0.0037
25	4.389	24510	0.0053		Formic acid.			23	4.765	58200	0.0035
30	4.393	24720	0.0048	0	4.635	43160	0.0015	30	4.772	60000	0.0033
40	4.400	25120	0.0039	20	4.665	46200	0.00135	35	...	...	...
50	4.411	25770	0.0036	26	4.670	46740	0.00125				
60	4.418	26200	0.0030	30	4.673	47060	...				
70	...	...	...	35	...	...					

TABLE II

Relation between time of saturation and dissociation constants of acids.

Acids.	Saturation time.	$K_{28}°$.
Formic	30 min.	2.14×10^{-4}
Acetic	30	1.36×10^{-5}
Benzoic	20	6.36×10^{-5}
Oxalic	30	3.8×10^{-2}
Malonic	20	1.61×10^{-3}
Succinic.	35	8.6×10^{-5}
Citric	24	8.2×10^{-4}
Phosphoric	60	1.1×10^{-2}

DISCUSSION

With a view to ascertaining some cause for the irregular adsorption of polybasic acids and regular adsorption of monobasic acids on sugar charcoal surface studied by Jain and Jha (*loc. cit.*), the study of the dissociation constants of various acids and their respective time of saturation on sugar charcoal was undertaken, and no relationship could be established between them, as shown in Table II. Further work is in progress in this direction. The rate of adsorption is generally found to increase with increasing amounts of charcoal. In the beginning the rate is rapid, then becomes slow. The time for saturation is not practically affected by increasing the amount of charcoal.

When the velocity constant (k) is calculated on the assumption of monomolecular reaction

$$k = 1/t \log e\, c/c - x$$

it is found that adsorption consists of two consecutive processes, the first, rapid and the second, slower, as shown in Table I.

The first goes on for a few minutes. The second course, when calculated on the monomolecular reaction equation, gives nearly constant values of velocity constant, although in some cases wide difference is seen in its values. The value of velocity constant falls off gradually and it shows that the reaction (adsorption) is reversible and takes time to attain equilibrium. Angelesen and Seoloviu (*loc. cit.*) on determining the rate of adsorption of oxalic and acetic acids on active charcoal came to similar conclusions, as none of the formulae hitherto proposed are valid over the whole interval.

The author is deeply indebted to Professor J. B. Jha of Agra College, and and Dr. W. V. Bhagwat of Holkar College, Indore for their kind interest in this work.

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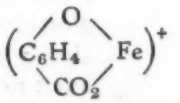
FERRIC COMPLEXES OF PHENOLS. PART III. β-RESORCYLIC ACID AND PYROGALLOL

By S. K. K. Jatkar and B. N. Mattoo

The ferric complexes of β-resorcylic acid have been studied potentiometrically and colorimetrically. A colorimetric titration gives a sharp break indicating 1 : 1 complex. The potentiometric titration indicates the complexes with Fe^{3+} : acid ratio equal to 1 : 2 and 1 : 3, in addition to the most prominent 1 : 1 complex. Structures for the three complexes are presented.

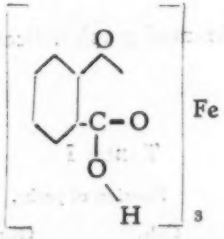
A colorimetric titration of aqueous pyrogallol at low concentration with $FeCl_3$ shows a sharp break at the mole ratio $1Fe^{3+}$: 2 pyrogallol.

β-Resorcylic acid (2:4-dihydroxybenzoic acid) like salicylic acid gives a stable purple-red colour with $FeCl_3$. Babko (*J. Gen. Chem. U. S. S. R.*, 1945, **15**, 745) reports the salicylic-ferric complex to be

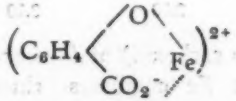


in acid solution ; while higher complexes FeR_2^- and FeR_3^{3-} have been reported at higher p_H. Illari (*Ann. Chim. Appl.*, 1940, **30**, 65) postulates the presence of $C_6H_4(O.FeCl_2).CO_2H$, the violet ferric-salicylic acid complex. In presence of $NaHCO_3$, a violet complex C_6H_4 [O.Fe $(OH)_2$].COOH and in presence of HCl, a more intensely coloured complex, $C_6H_4(O.FeCl_2).CO_2.FeCl_2$ have been reported. Sulphosalicylic acid in acid solution forms a complex with Fe^{3+} with 1:1 molar ratio of ferric to sulphosalicylic acid (Foley and Anderson, *J. Amer. Chem. Soc.*, 1948, **70**, 119).

It has been found in salicylic acid-ferric complexes, that Fe is held not by the acidic hydroxyl but by the phenolic hydroxyl (Sidgwick, "Chemical Elements and Their Compounds", 1950, p. 1363), because methyl ester forms a coloured compound with Fe^{3+}, but the methyl ether does not. The structure for the tri-acid complex is presented as



Kuznetzov (*J. Gen. Chem. U. S. S. R.*, 1950, **20**, 816) assigns the structure (I) to the violet ferric-salicylate complex, and not the structure as assigned by Babko (*loc. cit.*).

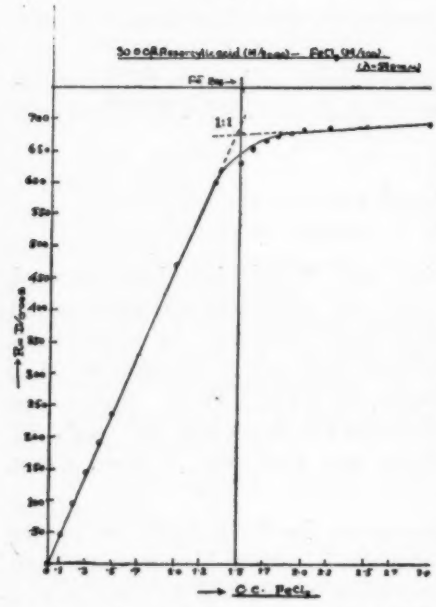


(I)

The present study deals with colorimetric and potentiometric study of β-resorcylic acid—$FeCl_3$ reaction.

EXPERIMENTAL

FIG. 1



Colorimetric Titration.—Aqueous *M*/2000-β-resorcylic acid (30 c.c.) was titrated with *M*/100-$FeCl_3$ in a 2 cm. cell of a Klett-Sommerson colorimeter. The absorption was measured at 540 mμ. Readings (corrected for dilution), when plotted against the amount of Fe^{3+} added, give a sharp break at 1:1 molar ratio of ferric to acid (Fig. 1).

Potentiometric Titration.—*M*/100-$FeCl_3$ (5 c.c.), diluted to 25 c.c. with distilled water, was titrated with *M*/20 β-resorcylic acid. The oxidation-reduction potential of Fe^{3+} ion in varying amount of the acid was measured, using the system :

$$\overset{+}{Pt} \mid \text{soln.} \mid \text{satd. KCl} \mid \textit{N}\text{-KCl-}\overset{-}{Hg_2Cl_2} \mid \overset{-}{Hg}$$

E. M. F. measurements were made on a Doran potentiometer. The inflexions in the c.c.-E. M. F. curve (graph I, Fig. 2) are brought out clearly in the differential graph (mean c. c. *vs.* $\Delta E/\Delta$ c.c.) (graph II, Fig. 2.)

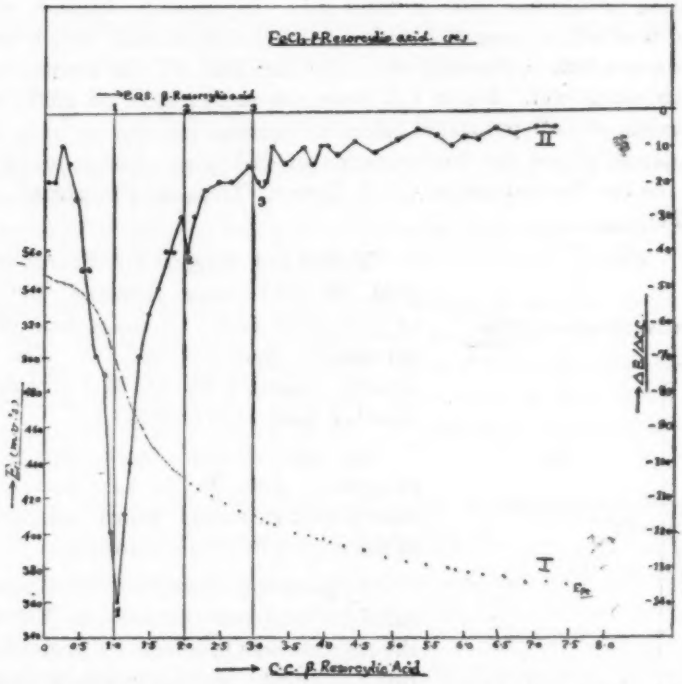
The sharp peaks in the differential graph indicate the following complexes.

TABLE I

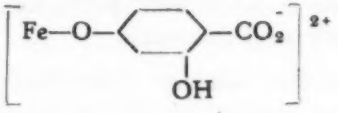
Fe^{3+} : β-resorcylic acid.	Position of peaks.		Relative intensity of peaks.
	Calc.	Obs.	
1 : 1	1.00	1.05	140
1 : 2	2.00	2.05	40
1 : 3	3.00	3.10	20

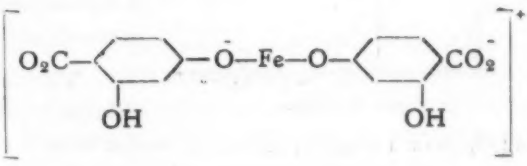
Only one hydroxyl (*para* to carboxyl) of β-resorcylic acid is found to dissociate ; so it may be concluded that Fe combines through this hydroxyl to form the coloured complex. The second hydroxyl group has been reported not

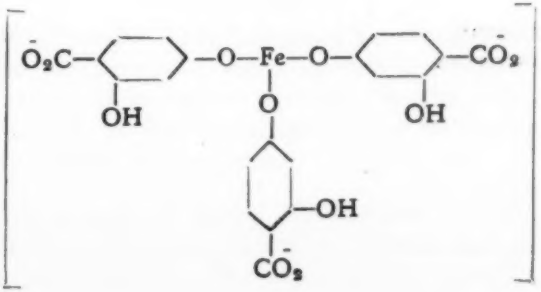
FIG. 2



to dissociate (Hukamanai, *J. Pharm. Soc. Japan*, 1940, **60**, 209). The following structures may therefore be assigned to the three complexes of ferric-β-resorcylic acid, which are indicated by the potentiometric study :

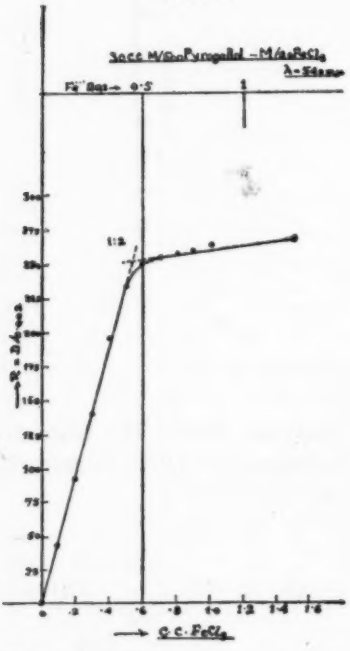






Pyrogallol-ferric Chloride.—Pyrogallol gives a green-blue colour with $FeCl_3$ in alcoholic solution (absorption max. in infra red). In aqueous solution, when dilute $FeCl_3$ solution is added to pyrogallol, a blue colour is first formed, which immediately changes to brownish yellow, showing obviously the shift of the absorption maxima from visible to ultraviolet. Brode (*J. Amer. Chem. Soc.*, 1934, **56**, 1037) reports the absorption maxima of Fe^{3+}-pyrogallol colour in aqueous solution to lie in ultraviolet. The reaction depends upon the concentration of Fe^{3+} also. Excess of Fe^{3+} oxidises pyrogallol to the dye Purpurogalline (Paul Karrer, "Organic Chemistry", translated by Mee, p. 421).

FIG. 3



Takagi and Nagase (*J. Pharm. Soc. Japan*, 1936, **56**, 161) have reported Bi^{3+} complex of pyrogallol with 1 : 1 molar ratio of metal to pyrogallol. Shuttleworth (*J. Soc. Leather Trade's Chem.*, 1948, **32**, 281) obtained a violet complex with $Cr(OH)SO_4$.

In the present work, the reaction of pyrogallol with $FeCl_3$ has been studied by colorimetric titration, which indicates a break of the ratio 1 Fe^{3+} to 2 pyrogallol.

Colorimetric Titration.—*M*/500 aqueous pyrogallol (30 c.c.) was titrated with *M*/20-$FeCl_3$ and the reaction was followed by measuring absorption at 540 mμ. Measurements at shorter wavelengths would have been desirable ; but in this region absorption of $FeCl_3$ (e.g. at 420 mμ) changed appreciably with time, therefore, such a wave-length was chosen at which $FeCl_3$ showed a steady and fairly good absorption.

The absorption readings (correcred for dilution) plotted against the amount of Fe^{3+} added, show a sharp break at the molar ratio 1 : 2 of Fe^{3+} to pyrogallol (Fig. 3).

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FERRIC COMPLEXES OF PHENOLS. PART IV. PONGAMOL AND ITS ESTIMATION IN KARANJA OIL

By S. K. K. Jatkar and B. N. Mattoo

The pongamol-ferric chloride reaction has been studied colorimetrically and evidence for 1 : 1 (Fe^{3+} : pongamol) complex obtained.

An estimation of pongamol in karanja oil, by making use of this reaction, gives a value of 0.7% as against 0.1% reported by previous workers. Authors have actually isolated 0.85% pongamol from the oil.

Pongamol was isolated in 0.1% yield on the weight of karanja oil by continuous extraction with methyl alcohol by Rangaswami and Seshadri (*Ind. J. Pharm.*, 1941, **3**, 3; *Proc. Ind. Acad. Sci.*, 1942, **15A**, 417). The analysis and molecular weight determination of this compound show that its formula is $C_{18}H_{14}O_4$, containing a methoxy and a hydroxyl group. The presence of the latter group gives rise to a stable, deep red coloration with $FeCl_3$.

The present paper records a colorimetric study of the ferric-pongamol coloured complex and an estimation of pongamol in the parent oil.

In the preceding papers of this series (this *Journal*, 1953, **30**, 592, 667, 775) it has been shown, as also by several previous workers, that phenols form a number of stoichiometric complexes with ferric ion, $Fe(OR)_n$, where -OR is the ionised phenol and n has values ranging from 1 to 6. In the case of phenols containing a carboxyl group in the aromatic ring, the mono-complex $Fe(OR)^{2+}$ is the most prominent. A colorimetric titration of alcoholic pongamol solution with alcoholic ferric chloride shows a sharp break at 1 : 1 ratio, indicating thereby the formation of ferric mono-pongamol complex.

The titration was carried out on the Klett-Sommerson photoelectric colorimeter; 30 c. c. of pongamol solution (0.02 g./150 c. c.) were titrated with *M*/200 alcoholic ferric chloride in a rectangular glass cell with 2 cm. path. Absorption was measured at 540 mμ. The graph plotted between the amount of Fe^{3+} added and the corresponding absorption (corrected for dilution and excess of the reagent) shows a sharp break at the composition, 1 Fe^{3+} : 1 pongamol (Fig. 1).

Estimation of Pongamol.—The pongamol-ferric colour being quite stable, obeying Beer's law in solution, it was of interest to estimate it in the karanja oil. The other constituents, such as karanjin etc., do not give any colour with $FeCl_3$. Prior to the determination, absorption spectrum of the complex was found on the Hilger-Spekkar photoelectric absorptiometer.

Pure pongamol solution in alcohol (0.0202 g./100 c.c.) was taken; 0.1 c.c. of *M*/20 alcoholic $FeCl_3$ was added to 5 c.c. of the solution, which was then stirred well before measuring the absorption. The absorption *vs.* wave-length is plotted in

Fig. 2, the maximum being at 517 mμ. The slight excess of $FeCl_3$ has no appreciable effect on the optical density of the complex at the wave-length of maximum absorption.

FIG. 1

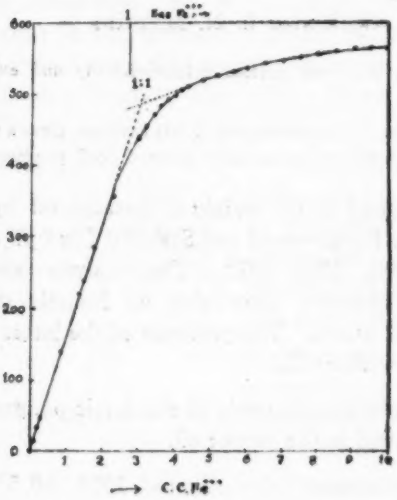
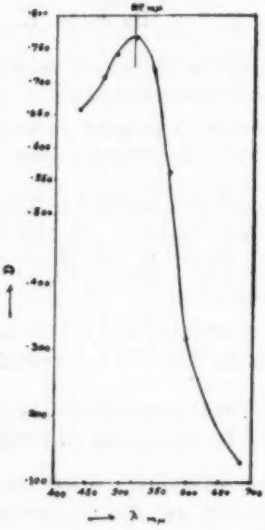


FIG 2.



For the estimation, the optical density was measured at the maximum absorption. 1.031 G. of karanja oil was extracted with cold 90% alcohol by shaking it vigorously and allowing the emulsion to separate into two layers by centrifuging. On centrifuging, the oily layer settled down and the clear alcoholic extract was poured off and collected. The oil was extracted four times with fresh portions of the solvent, and the extract was finally made up to 50 c.c.

The standard solution of pongamol (5 c. c., 0.0202 g./100 c. c.) and the alcohol extract were taken in two identical 1 cm. cells ; 0.2 c. c. of *M*/20 EtOH- ferric chloride was added to each solution. The optical density of the standard solution was found to be 0.7915 and that of the alcohol extract was 0.5480. The percentage thus found is about 0.7% pongamol on the weight of the oil.

This value is considerably higher than 0.1%, reported by Seshadri (*loc. cit.*) in his samples of the oil. We therefore extracted karanja oil from local seeds and obtained as much as 0.85% pongamol. The details of the isolation will be published elsewhere.

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THE COMPONENT ACIDS OF REFINED KARANJA OIL. (*PONGAMIA GLABRA*, VENT)

By S. S. Gupta and C. R. Mitra

The component fatty acids of *karanja* oil (*Pongamia glabra*, Vent), freed of the non-fatty constituents and subsequently refined, deodorised and bleached after the processes evolved in the National Chemical Laboratory, have been analysed making use of low temperature crystallisation and spectrophotometric analytical methods. The fatty acid composition (percentage) of the purified and refined oil is: myristic, 1.6; palmitic, 7.9; stearic, 3.7; arachidic, 2.5; behenic, 4.2; lignoceric, 1.1; oleic, 62.1; linoleic, 11.9 and linolenic, 5.0. Dihydroxystearic acid, reported by earlier workers to be present in the oil, has not been found during the present stuidies.

Karanja oil, also known as *Hongay* oil, is obtained from the seeds of *Pongamia glabra*, Vent (N. O. Leguminoseae) in about 30% yield. The oil is dark coloured with a disagreeable taste and odour and is reputed to possess medicinal properties. The availability of *karanja* seeds appears to be comparatively considerable, particularly in Southern and Western India, but because of its dark colour and unpleasant odour and taste, the oil has hitherto found little use for soap making and other industrial purposes. A number of attempts have been made to refine the oil so as to render it suitable for utilisation in soap stock. Desai, Sudborough and Watson (*J. Ind. Inst. Sci.*, 1923, V, p. 91) tried the use of strong acid or strong alkali to remove the colouring matter and other non-fatty constituents from *karanja* oil, and they carried out a fairly detailed acid analysis of such treated oil. Some unusual features of their results were the reported presence of 4.5% of dihydroxystearic acid and absence of any behenic acid in the higher saturated components, which they reported to consist of arachidic and lignoceric acids only. In a subsequent communication, Manjunath and Shankara Rao (this *Journal*, 1938, 15, 653) claimed to have isolated behenic acid from the mixed acids of *karanja* oil, which, as they remarked, was not detected by Desai *et al.* (*loc. cit.*). No further work seems to have been carried out in regard to the composition of this oil.

Recently, processes more or less similar to those evolved in the case of *nim* oil for isolation of its active bitter constituents and subsequent refining of the oil (Siddiqui and Mitra, *J. Sci. Ind. Res.*, 1945, 4, 5; Ind. Pat. No. 33649 and 33650/1946), have been successfully adopted for refining of *karanja* oil in this laboratory (Mitra, Ind. Pat. No. 47802/1952). The process mainly consists in alcohol extraction of the oil in cold to remove most of the non-glyceridic constituents, and subsequent alkali refining and deodorisation. The refined oil so obtained was pale yellow in colour, without any foul smell or disagreeable taste, thus ensuring its suitability for industrial exploitation, and hence, it was thought of much interest to carry out a detailed analysis of this refined oil with the aid of the recently developed methods of low temperature crystallisation and spectrophotometric analyses of linoleic and linolenic acids (Hilditch, Morton, and Riley, *Analyst*, 1945, 70, 68; Crawford and Hilditch, *J. Sci. Food & Agric.*, 1950, 1, 230, 372; Gupta and Mitra, *ibid.*, 1953, 3, 44).

EXPERIMENTAL

The refined oil used in the present study had the following characteristics : I. V., 87.9 ; S. E., 295.3 ; acetyl value, 9.3 ; F.F.A., 0.2% (as oleic) ; unsaponifiable, 1.1%.

The oil (100 g.) was saponified, the unsaponifiable matter removed by extraction with ether and the mixed fatty acids obtained from the soap solution in the usual manner. The mixed acids (79.4 g.) were taken in dry ether (397. c.c.) and the solution kept at -20° (in a Defreez) overnight. The deposited acids were separated by filtration when the following acid fractions were obtained :

Fraction.	Condition.	Yield.	I. V.
A	Insol. in ether (×5) at -20°	12.4 g. 15.6%	9.6
B	Sol. „ „ „ „	67.0 . 84.4	105.9

These acid fractions were separately esterified with methanol containing 1% sulphuric acid (conc.) and the corresponding methyl esters distilled through an E. H. P. column under reduced pressure (*ca.* 0.5 mm). By carrying out the operation slowly and cautiously and taking conveniently small fractions, it is possible to obtain fractions containing not more than two homologous saturated acids together with two unsaturated acids of the same series, whose respective amounts can be calculated from the iodine value and saponification equivalent of the particular fraction (Hilditch, "Chemical Constitution of Natural Fats", 1947, 2nd Ed., p. 465). The fractionation analytical data along with the calculated composition of the different fractions from the insoluble and soluble acids are reproduced in Table I and Table II respectively.

Prior to computing the results in the case of fraction B, the respective amounts of the diethenoid and triethenoid acids in this fraction were determined spectrophotometrically according to the method recommended by Hilditch, Morton and Riley (*loc. cit.*). For that purpose, the fraction B_7 having the maximum unsaturation (I. V. 110.0) was selected and the corresponding acids recovered. Samples of these acids (0.1 g.) in duplicate were separately isomerised in glycolic potash solution at 180° and 170° for 60 minutes and 15 minutes respectively, the contents diluted with absolute alcohol to 250 c. c. and left overnight at 0°. After filtration and further appropriate dilution required to ensure optimum transmission density (0.4-0.6), at the particular wave-lengths, the solutions were examined in a Beckman spectrophotometer at 234 mμ and 268 mμ respectively, and the corresponding amounts of linoleic and linolenic acids in the fraction were calculated from the respective extinction coefficients at these wave-lengths. The spectrophotometric data and the composition of the fraction B_7 (I. V. 115.5) obtained therefrom are given below :

$E^{1\%}_{1\,cm.}$ at 268 mμ (170°-15 mins.) = 36

$E^{1\%}_{1\,cm.}$ at 234 mμ (180°-60 mins.) = 175

Whence the percentage composition of fraction B_7 is calculated as : saturated, 0.47 ; oleic, 77.80 ; linoleic, 15.24 and linolenic, 6.49.

Since these three unsaturated acids belong to the same series, thus not differing very much in the molecular weights, it can be assumed that their proportions are little

altered during distillation, and as such they would be present more or less in the same ratio in each fraction. On the basis of this assumption, which has already been verified (*loc. cit.*) to hold good in such analyses, oleic, linoleic and linolenic can be considered to be distilling as a mixture of fairly constant composition (oleic 78.17%, linoleic 15.31% and linolenic 6.52% as calculated from the composion of fraction B_7), and hence, their respective amounts in other fractions are calculated accordingly.

TABLE I

Fractionation of methyl esters of acids 'A'.

No.	Wt.	Temp.	S. E.	I. V.	Saturated C_{16}.	Saturated C_{18}.	Saturated C_{20}.	Saturated C_{22}.	Saturated C_{24}.	Oleic.
A_1	1.44 g.	120-130°	272.6	8.3	1.29	0.01	...	...	...	0.14
A_2	1.82	„ „	279.5	14.5	1.13	0.38	...	...	...	0.31
A_3	2.38	130-140°	299.3	16.0	...	1.77	0.16	...	...	0.45
A_4	1.85	140-150°	332.5	3.6	...	...	1.22	0.55	...	0.08
A_5	1.56	Column washings.	344.1	2.1	...	...	0.44	1.08	...	0.04
*A_6	2.27	Residue.	360.7	2.9	...	...	...	1.42	0.77	0.08
	11.32		Weights :		2.42	2.16	1.82	3.05	0.77	1.10
			% Esters :		21.4	19.1	16.1	26.9	6.80	9.70
			% Acids :		21.2	19.0	16.1	27.1	6.90	9.70

* No unsaponifiable matter traced.

TABLE II

Fractionation of methyl esters of acids 'B'.

[C_{18} unstd. esters (spectrophotometic) as S. E., 295.4 ; I. V., 110.6].

Fraction.	Wt.	Temp.	S. E.	I. V.	Saturated C_{14}.	Saturated C_{16}.	Saturated C_{18}.	Ol.	Lin.	Len.	N-S.
B_1	1.76 g.	130-135°	279.9	73.6	0.33	0.26	...		1.17		...
B_2	3.42	135-136°	286.4	88.4	0.33	0.36	...		2.73		...
B_3	3.90	136-139°	286.9	94.8	...	0.56	...		3.34		...
B_4	4.18	139-140°	290.8	100.0	...	0.40	...		3.78		...
B_5	5.22	140-145°	293.7	106.9	...	0.17	...		5.05		...
B_6	3.99	„	293.9	109.6	...	0.03	...		3.96		...
B_7	5.77	„	293.1	110.0	...	0.03	...		5.74		...
B_8	4.21	„	295.1	109.4	...	0.04	...		4.17		...
*B_9	2.82	Residue	302.8	95.4	...	0.09	0.29		2.42		2.02
	35.27		Weights :		0.66	1.94	0.29	25.30	4.95	2.1	2.02
			% Esters :		1.9	5.5	0.8	71.7	14.0	6.0	0.1
			% Acids :		1.9	5.5	0.8	71.7	14.0	6.0	0.1

* B_9 acids ex. N-S, S. E. 279.4.

From the computed data for fractions A and B shown in Table I and Table II, the percentage composition of the component fatty acids in the oil was deduced as shown in Table III.

TABLE III

Acids.	Fraction A (15.6%).	Fraction B (84.4%).	Total (% wt.).	(% mol.).
Myristic	...	1.56	1.56	1.93
Palmitic	3.31	4.62	7.93	8.73
Stearic	2.97	0.69	3.66	3.63
Arachidic	2.51	...	2.51	2.26
Behenic	4.23	...	4.23	3.50
Lignoceric	1.07	...	1.07	0.82
Oleic	1.51	60.60	62.11	62.06
Linoleic	...	11.88	11.88	11.95
Linolenic	...	5.05	5.05	5.12

Identification of Individual Fatty Acids : Linoleic and Linolenic Acid.—Acids from the most unsaturated fraction (B_7) were subjected to bromination at 0°, when fairly pure crystalline samples of hexabromostearic acid (m.p. 179-80°, mixed m. p. with an authentic sample, 179°), and tetrabromostearic acid (m. p. 113-14° ; mixed m. p. with an authentic sample, 113-14°) were obtained, and thus, the polyethenoid acids were identified to be the ordinary seed fat type linoleic and linolenic acids found in most vegetable fats.

Higher Saturated Acids.—As mentioned earlier, on the basis of a substantial acetyl value (20-24) exhibited by the oil and high refractive index of particular fractions, Desai *et al.* (*loc. cit.*) suggested the presence of about 4.5% of dihydroxystearic acid in *karanja* oil. During their study of castor oil, Gupta, Hilditch and Riley (*J. Sci. Food. & Agric.*, 1951, 2, 245) found that dihydroxystrearic acid present in castor oil could be almost quantitatively separated from the mixed acids by deposition from a 10% solution in ethyl acetate at 0°. The sample of *karanja* oil used during the present analysis yielded by such treatment white crystalline fatty acids melting at 84-85°. The melting point could not be raised any further by subsequent crystallisation, and as such there seems to be no hydroxystearic acid in *karanja* oil. The most insoluble acid fraction, referred to above, was identified as lignoceric acid.

DISCUSSION

The results of the present investigation have revealed that *karanja* oil is very similar in composition to other fats belonging to the Leguminoseae family, and apart from the usual saturated and unsaturated acids, contains 7-8% of higher saturated (C_{20}-C_{24}) acids. As mentioned earlier, there is no indication of the

presence of any dihydroxystearic acid in contrast to the observation of Desai *et al.* (*loc. cit.*), and the acetyl value exhibited by the oil is most probably due to the presence of impurities and/or mono- and di-glycerides. This belief is amply justified by the fact that the acetyl value is considerably reduced after refining of the oil. In this connection, it may be further added that Desai *et al.* also could not isolate any dihydroxystearic acid from the oil. Moreover, the amount of dihydroxystearic acid recorded by them did nof fully account for the observed acetyl value (22) which can only be explained as being due to other factors, referred to above.

Table IV affords a comparison of the acid composition of *karanja* oil as determined in the present study with two other important Leguminous seed fats.

TABLE IV

Component acids.	Karanja oil (a). (*Pongamia glabra* Vent).	Groundnut oil (b). (*Arachis hypogaea*).	Pentaclethra fats (c)	
			P. mycrophylla.	*P. Eetueldeana.*
C_{14} (satd.)	1.6	...	...	...
C_{16}	7.9	8.5	5.2	3.7
C_{18}	3.7	4.4	4.3	4.8
C_{20}	2.5	6.6	2.6	4.8
C^{22}	4.2		5.8	13.9
C_{24}	1.1		13.1	2.8
Oleic	62.1	54.0	20.3	53.3
Linoleic	11.9	26.0	48.7	16.1
Linolenic	5.0	...	...	...

(a) Present study.
(b) Hilditch and Riley, *J. Soc. Chem. Ind.*, 1945, 64, 204.
(c) Hilditch, Meara and Patel, *J. Sci. Food. & Agric.*, 1951, 2, 142.

The close similarity of composition in case of *karanja* and groundnut oils is suggestive of the prospective utilisation of the former in soap stock.

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POTENTIOMETRIC STUDIES IN OXIDATION-REDUCTION REACTIONS. PART XV. OXIDATION WITH POTASSIUM METAPERIODATE. IODINE BROMIDE METHOD

By Balwant Singh and Apar Singh

Potassium metaperiodate has been used as an oxidising agent in acid medium in presence of a large excess of bromide ion for the potentiometric estimations of potassium iodide, tartar emetic, ferrous sulphate, potassium sulphocyanide, sodium thiosulphate, sodium tetrathionate, hydrazine sulphate, hydroquinone and stannous chloride by the iodine bromide method.

Potassium metaperiodate in acid solution is a strong oxidising agent and is reduced to iodine :

$$2\,IO_4^- + 16H^+ + 14e = I_2 + 8H_2O.$$

The iodine is further oxidised by the periodate

$$3\,I_2 + IO_4^- + 8H^+ = 7\,I^+ + 4H_2O.$$

Iodine cation forms a stable iodine bromide complex in presence of a high concentration of bromide ion.

$$I^+ + 2\,Br^- = IBr_2^-.$$

This method is therefore based on titration in acid medium with potassium metaperiodate in presence of a large excess of potassium bromide. The periodate reacts in accordance with the following equations :

$$3\,I^- + IO_4^- + 8H^+ + 8\,Br^- = 4\,IBr_2^- + 4\,H_2O.$$
$$3\,Sb_2O_3 + 2\,IO_4^- + 4H^+ + 4\,Br^- = 3\,Sb_2O_5 + 2\,IBr_2^- + 2\,H_2O$$
$$6\,Fe^{2+} + IO_4^- + 8\,H^+ + 2\,Br^- = 6\,Fe^{3+} + IBr_2^- + 4\,H_2O$$
$$CNS^- + IO_4^- + 2\,Br^- = SO_4^{2-} + IBr_2^- + CN^-$$
$$3\,S_2O_3^{2-} + 4\,IO_4^- + 2\,H^+ + 8\,Br^- = 6\,SO_4^{2-} + 4\,IBr_2^- + H_2O$$
$$3\,S_4O_6^{2-} + 7\,IO_4^- + 14\,Br^- + 2\,H_2O = 12\,SO_4^{2-} + 4\,H^+ + 7\,IBr_2$$
$$3\,N_2H_4 + 2\,IO_4^- + 4\,H^+ + 4\,Br^- = 3\,N_2 + 2\,IBr_2^- + 8\,H_2O$$
$$3\,C_6H_4(OH)_2 + IO_4^- + 2\,H^+ + 2\,Br^- = 3\,C_6H_4O_2 + IBr_2^- + 4\,H_2O$$
$$3\,Sn^{2+} + IO_4^- + 8\,H^+ + 2\,Br^- = 3\,Sn^{4+} + I\,Br_2^- + 4\,H_2O$$

Experimental

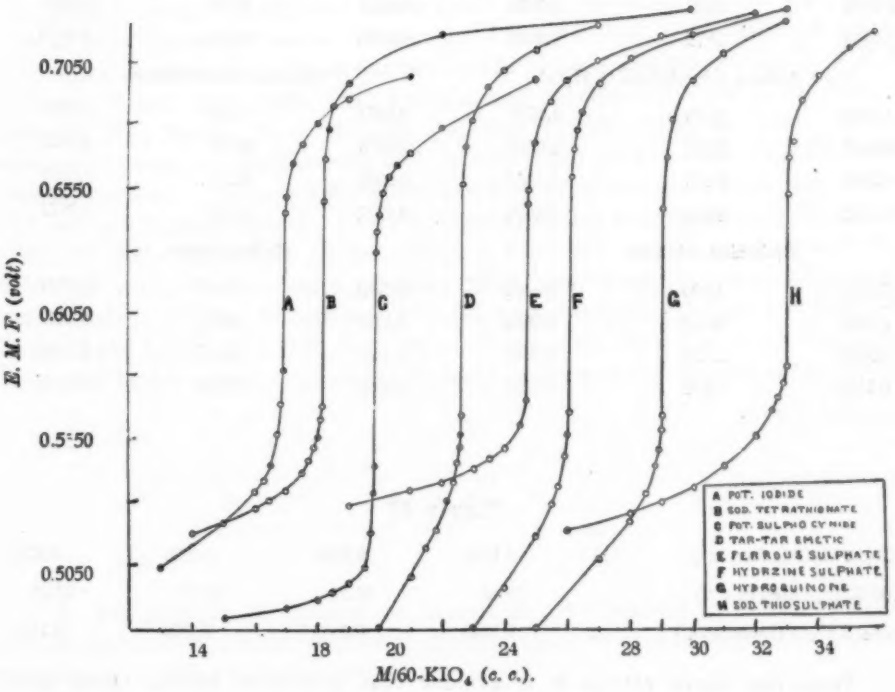
Potassium metaperiodate was prepared by the method of Bahl and Singh (this *Journal*, 1940, 17, 167).

The oxidation—reduction electrode, which consisted of a bright platinum foil immersed in a solution to be titrated, was coupled with a saturated calomel electrode through an agar-agar potassium chloride bridge. The cell was placed in a water-bath, temperature of which was maintained at 20°. E.M.F. of the cell was read on a potentiometer.

A known weight of each substance was mixed with 20 c.c. of water, about 20 to 25 g. of potassium bromide and 5 c.c. of concentrated hydrochloric acid, and titrated against standard potassium metaperiodate solution. In these titrations normality of the solution with respect to hydrochloric acid was kept between 1 and 2 and the mixture was kept stirred by a mechanical stirrer.

The titrations, one for each substance, are represented by the curves shown in Fig. 1.

FIG. 1



DISCUSSION

In these titrations it is evident that with the addition of the titrant the E.M.F. rose steadily till the equivalence point. At the equivalence point there was a sharp jump in potential followed by a steady rise in each case.

From the amount of potassium metaperiodate used, corresponding to the equivalence point in each titration, the amount of each substance was calculated. In the following tables the calculated values are compared with the amounts of the substances taken.

TABLE I

Taken.	$M/60$-KIO_4 used.	Found.	Taken.	$M/60$-KIO_4 used.	Found.
	Pot. iodide.			Tartar emetic.	
0.1411 g.	16.95 c.c.	0.1407 g.	0.2589 g.	15.50 c.c.	0.2589 g.
0.1851	23.00	0.1851	0.3791	27.70	0.3791
0.2241	26.95	0.2237	0.5653	33.85	0.5653
	Ferrous sulphate (7 H_2O).			Potassim sulphocyanide.	
0.0350	12.55	0.0349	0.0275	17.05	0.0276
0.0584	20.95	0.0582	0.0323	19.90	0.0322
0.0689	20.75	0.0688	0.0436	26.90	0.0435
	Sodium thiosulphate (5 H_2O).			Sodium tetrathionate.	
0.0527	16.95	0.0525	0.0351	18.20	0.0351
0.0620	20.00	0.0620	0.0473	24.05	0.0473
0.0840	27.15	0.0842	0.0602	31.20	0.0602
0.1023	33.05	0.1025	0.0772	40.05	0.0773
	Hydrazine sulphate.			Hydroquinone.	
0.0455	14.00	0.0455	0.0743	13.40	0.0737
0.0650	20.10	0.0653	0.1100	20.20	0.1111
0.0845	26.15	0.0849	0.1595	29.10	0.1601
0.1105	33.95	0.1103	0.2035	37.15	0.2043

TABLE II

$SnCl_2$, 2 H_2O (taken in g.)	...	0.1740	0.2068	0.2526	0.3125
$M/60$-KIO_4 (used in c.c.)	...	15.40	18.30	22.35	27.65
$SnCl_2$, 2 H_2O (found in g.)	...	0.1740	0.2068	0.2526	0.3124

From the above results it is evident that potassium iodide, tartar emetic, ferrous sulphate, potassium sulphocyanide, sodium thiosulphate, sodium tetrathionate, hydrazine sulphate, hydroquinone and stannous chloride can be determined potentiometrically by the iodine method, using potassium metaperiodate as an oxidising agent in acid medium.

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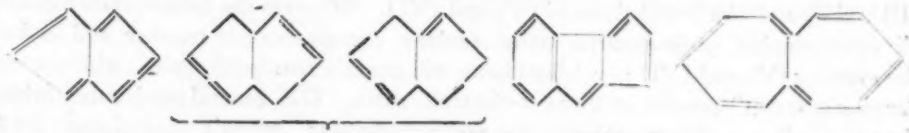
AZULENES AND RELATED SUBSTANCES. PART III. STUDIES IN *cyclo*HEPT[f]-INDENE

By Sukh Dev

The possibilities of the existence of a system (V) have been discussed and the firstexperiments towards its synthesis have been described.

Armit and Robinson (*J. Chem. Soc.*, 1922, **121**, 828) postulated pentalene (I) as a possible aromatic compound, but it could not be prepared by the dehydrogenation of its octahydro derivative (Barrett and Linstead, *ibid.*, 1936, 612). A quantum mechanical study of the problem has been made by Craig and Maccoll (*ibid.*, 1949, 964; also see Baker, *ibid.*, 1945 258; Coulson and Rushbrooke, *Proc. Camb. Phil. Soc.*, 1940, **36**, 193; Brown, *Trans. Faraday Soc.*, 1949, **45**, 296; 1950, **46**, 146). A recent attempt to prepare pentalene from (II) has also failed (Roberts and Gorham, *private communication*). The only known derivatives of pentalene are the complex diphenyl and dichloro derivatives of 1 : 2 : 4 : 5-dibenzpentalene (see Brand and Hennig, *Ber.*, 1948, **81**, 382, 387). The recent chemical literature reveals much activity in this field and various unsuccessful attempts have been made to prepare the systems benzpentalene (III)* and heptalene (IV) (Horn and Rapson, *J. Chem. Soc.*, 1949, 2421; Aspinall and Baker, *ibid.*, 1950, 743). Brown (*ibid*, 1951, 2391) has contributed a paper on the molecular orbital calculations for some aromatic hydrocarbons of the type :



(I) (II) (III) (IV)

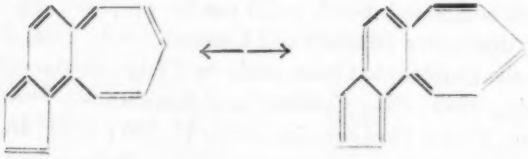
It was thought of interest to investigate the possible synthesis of some new type of such systems, which may have greater chances of existence. This communication deals with such attempts.

Two systems, (V) and (VI), were selected for consideration. In these cases a benzene ring has been interposed between 5- and 7-membered rings. It is interesting to note that in (III) and (VII) (see Brown, *loc. cit.*), in a way, pentalene system occurs which has evaded all attempts at synthesis; whereas (V) and (VI) will contain in the same way the azulene system. Azulene and its derivatives are well known and several of these occur in nature (*Ann. Reports*, 1947, **44**, 162; Elsevier's Encyclopaedia of Organic Chemistry, Vol. 12A, pp. 420-442, 1948; Pommer, *Z. angew.*

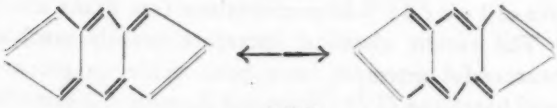
*Also termed *cyclo*pentindene (Baker and Leeds, *J. Chem. Soc.*, 1948, 974; Baker and Jones, *ibid.*, 1951, 787; Baker, Glockling and McOmie, *ibid.*, 1951, 3357; Clemo, Groves, Munday and Swan, *ibid.*, 1951, 863; Groves & Swan, *ibid.*, 1951, 867 and Dahn, *Helv. Chim. Acta*, 1951, 34, 1087).

Chem., 1950, **62**, 281 : Haagen-Smit, "Progress in the Chemistry of Organic Natural Products", 1948, **5**, 40 ; Gordon, *Chem. Rev.*, 1952, **50**, 127) and the system possesses considerable aromaticity (Gordon, *loc. cit.*, p. 182). Here the systems (V) and (VII) might be imagined as derived from azulene by interposing a six-membered ring which may be regarded as a "resonance link" between the 5- and 7-membered rings.

(V)



(VI)



(VII)

There appears to be one fundamental difference between compounds of type (I), (III), (IV) and (VII) and those of (V) and (VI). Whereas the former class contains all even number of π-electron pairs, azulene contains an odd number, and so does the systems (V) and (VI) ; *cyclo*butadiene will contain two such pairs, whereas the "aromatic sextet" consists of three π-electron pairs. The general molecular orbital theory ascribes peculiar stability to cyclic molecular orbitals containing $2+4n$ electrons (Hückel, "Grundzuge der Theorie ungesättiger und aromatischer Verbindingen", Verlag Chemie, Berlin, 1938, pp. 77-85).

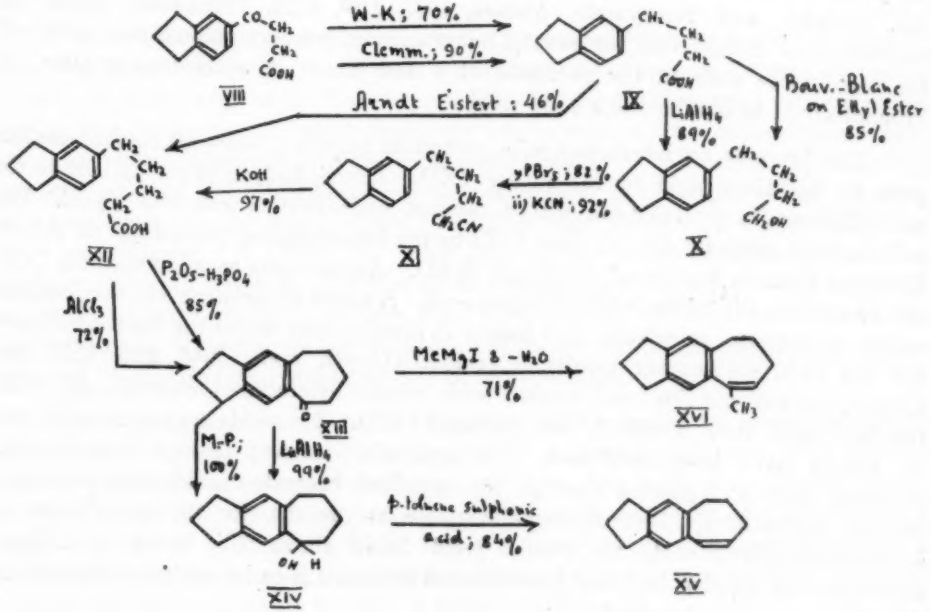
Whereas system (V) has two equivalent most stable contributing structures (a) and (b), (VIa) and (VIb) on the other hand are not equivalent, and on this account (V) might be expected to be more stable than (VI). Therefore routes to (V) have been firstly explored.

The substance (V) would be a completely conjugated cyclic polyolefin and the molecule will be flat, so that the overlapping of p-orbitals will be maximum, and as such might be expected to possess considerable resonance energy (Syrkin and Dyatkina, "Structure of Molecules", London, 1950).

The synthesis of (V) has been attempted along the lines indicated below :

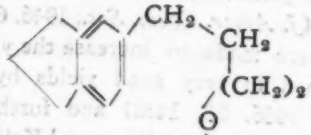
β-5-Hydrindoylpropionic acid (VIII) has been prepared by several workers (Fieser and Seligman, *J. Amer. Chem. Soc.*, 1937, **59**, 883, 97% ; cf. Fieser *et al.*, *ibid.*, 1948 **70**, 3200 ; Sengupta, this *Journal*, 1939, **16**, 89, 42% ; McQuillin and

Robinson, *J. Chem. Soc.*, 1941, 586, 87% ; Plattner, Fürst and Keller, *Helv. Chim. Acta*, 1949, **32**, 2464, 77%). The procedure described in the experimental is more convenient and gives the best yields. The Wolff-Kishner reduction of the keto-acid according to Huang-Minlon (*J. Amer. Chem. Soc.*, 1946, **68**, 2487) furnished (IX) in 70% yield. No attempts were made to increase the yield by this process, as the compound could be obtained in very good yields by Clemmensen reduction, as modified by Martin (*ibid.*, 1936, **58**, 1438) and further improved by Sherman (cf. Fieser *et al. loc. cit.*, p. 3197). Plattner, Fürst and Keller (*loc. cit.*) have carried out the Clemmensen reduction on the ethyl ester.



The acid (IX) could be smoothly reduced to the alcohol (X) with lithium aluminium hydride by the general procedure of Nystrom and Brown (*J. Amer. Chem. Soc.*, 1947, **69**, 2548). The ethyl ester of the acid could also be reduced in a very good yield by the modified Bouveault-Blanc method (Hansley, *Ind. Eng. Chem.*, 1947, **39**, 55). The corresponding bromide was prepared by the action of phosphorus tribromide on the alcohol. When the reaction was carried out for several hours at -15° to 0° and then for three hours at room temperature (24°), about two third of the alcohol was recovered unchanged and a higher boiling residue was left which on attempted distillation under vacuum (1.5 mm.) underwent decomposition to yield a low boiling material and a phosphorus containing residue was left in the flask,

which ignited when exposed to air, while still warm. It is quite likely that a complex like



(XVII) Br—P—Br

is produced which is unusually stable and on heating undergoes decomposition to yield a hydrocarbon (b. p. 90°-120°/1.5 mm. ?), alcohol and traces of bromide (cf. Gerrard and Nechvatal, *Nature*, 1947, **159**, 812). However, when the reaction was carried out for several hours at room temperature and then at 60°-65° for some more time in the presence of a few drops of anhydrous pyridine, the bromide could be obtained in a good yield.

The bromide on interaction with potassium cyanide in aqueous alcohol medium gave an excellent yield of the nitrile (XI). The hydrolysis of the cyanide to the acid (XII) was best carried out with potassium hydroxide in ethylene glycol. The acid was also prepared directly from (IX) by the homologation procedure of Arndt-Eistert ("Organic Reactions", Vol I, pp. 38-62). An alternate route to the acid (XII) can be through the γ-5-hydrindoylbutyric acid. A single experiment on the condensation of glutaric anhydride with indane in nitrobenzene under the usual conditions did not yield satisfactory results. Cagniant (*Compt. rend.*, 1948, **226**, 1623) has however, carried out this condensation with monoethylglutaroyl chloride and from the keto-acid, then obtained, has prepared (XII). But yields are not reported and no details have been published. The synthesis, starting from β-5-hydrindoylpropionic acid and passing through the standard bromide-cyanide-acid sequence, perhaps, represents the best procedure available, at present, for the preparation of δ-5-hydrindylvaleric acid, the overall yield being above 50% based on indane. However, for smaller lots, the Arndt-Eistert synthesis is to be preferred because of the economy in time involved.

Cagniant (*loc. cit.*) has reported the cyclisation of the acid (XII) to the corresponding ketone, but no details have been published. The ketone can be readily prepared by the intramolecular ring-closure of the acid chloride using a procedure similar to that employed by Plattner (*Helv. Chim. Acta*, 1944, **27**, 804) for the preparation of benzosuberone. However, use of a large volume of carbon disulphide can be avoided by employing the dilution apparatus, as modified by Cope and Herrick (*J. Amer. Chem. Soc.*, 1950, **72**, 985). Gilmore and Horton (*ibid.*, 1951, **73**, 1413; also see Gilmore, *ibid.*, 1951, **73**, 5879) have described the preparation of benzosuberone from δ-phenylvaleric acid by its cyclisation with phosphorus pentoxide-phosphoric acid reagent. The reagent appears to be eminently suited for such ring-closures, resulting in the formation of new 5-, 6- or 7-membered rings. Under these conditions the acid (XII) smoothly undergoes cyclisation to yield the ketone

(XIII) in over 85% yield. The ketone readily gives a red 2 : 4-dinitrophenylhydrazone, which appears to be polymorphous ; it can be obtained either in long, flat, shining needles or in ruby-red, short prisms. The latter form appears to be more stable and a solution from which needles have crystallised out, if allowed to remain as such for some days, may ultimately deposit minute prisms, with the disappearance of the needles ; however, both forms have the same m.p. and exhibit no depression in m.p. on admixture (cf. the behaviour of 2:4-dinitrophenylhydrazone of *n*-hexylphenyl ketone : Braddock and Willard, *ibid.*, 1951, 73, 5867).

The ketone has been reduced to the alcohol (XIV) both by lithium aluminium hydride and Meerwein- Ponndorf reaction. Both methods gave practically quantitative yields of the carbinol.

The dehydration of the alcohol to the corresponding unsaturated hydrocarbon has been accomplished by azeotropic distillation of a benzene solution with a trace of *p*-toluenesulphonic acid. Other methods of dehydration gave unsatisfactory results. To arrive at the best procedure and to work out the optimum conditions for dehydration, pilot experiments were carried out on benzosuberol. This alcohol was prepared by the Meerwein-Ponndorf reduction of benzosuberone ; $LiAlH_4$ reduction gave equally good results. Recently, this alcohol has been prepared by Horn and Rapson (*J. Chem. Soc.*, 1949, 2421) by the action of sodium and alcohol in moderate yield. These authors also carried out its dehydration to benzosuberene by fused potassium hydrogen sulphate, but yields were not satisfactory. Incidentally, the Oppenauer oxidation of benzosuberol was carried out, when a mixture of benzosuberene (41.6%) and benzosuberone (37.5%) was obtained.

The dehydrogenation of the hydrocarbon (XV) has been attempted by its passage over 30% Pd-C catalyst in the vapour phase under vacuum. The product was systematically chromatographed over alumina, but none of the desired hydrocarbon (V), which should be deeply coloured, and should be capable of forming complexes with T.N.B. etc., could be isolated. Similarly the methyl analogue (XVI) could not be dehydrogenated, either with sulphur, chloranil or catalytically. Stepwise introduction of double bonds in (XV) is being investigated.

EXPERIMENTAL*

β-(5-Hydrindoyl)-propionic Acid (VIII).—Indane was prepared and purified as described in the earlier paper (Sukh Dev, this *issue*, p. 729).

Indane (59 g., 0.5*M*), succinic anhydride (55 g., 0.55*M*) and dry nitrobenzene (200 c.c.) were placed in a 2-litre 3-necked flask, carrying a slip-sealed stirrer and a $CaCl_2$ exit-tube. The mixture was chilled in ice-salt and with stirring introduced

* All melting and boiling points are uncorrected. Measurements of pressure are by a vacustat. Analyses by Mr. Sitaramia.

anhydrous aluminium chloride (146.3 g., 1.1 *M*) in four lots during 1½ hours. The reaction mixture was stirred at the ice-bath temperature for 3 hours and then replenished the ice-bath and left aside overnight (12 hours). Next day, it was again stirred at room temperature (26°) for six hours, and the dark, viscous reaction mixture was poured on to ice and hydrochloric acid (150 c. c.). After adding 200 c. c. of ether, the solvent layer was separated ; aqueous part was extracted with ether (100 c. c. × 2) and the extracts mixed with the main portion, which was further diluted with 100 c. c. of benzene. It was washed with dilute hydrochloric acid (1 : 1 ; 100 c. c. × 3) and water (200 c. c. × 2) and finally extracted with dilute cold NaOH solution (4% ; 250 c. c. × 3). The dark alkaline extract was washed once with benzene (200 c. c.) and acidified with cooling with concentrated hydrochloric acid (Congo red). The separated acid was purified by dissolving in Na_2CO_3 solution, followed by a norit treatment and acidification ; yield of a product of m.p. 116-19° was quantitative. It was recrystallised from dilute acetic acid (200 c. c. of acetic acid and 400 c. c. of water) with a norit treatment, yielding white prisms, m.p. 119-23°, yield 100 g. (91.8%). A sample was again crystallised from dilute acetic acid and then from dilute alcohol, when the acid was obtained as white, long, prismatic needles, m.p. 124.5-25.5° (Fieser and Seligman, *loc. cit.*, give m.p. 125-25.5°).

γ-(5-*Hydrindyl*)-*butyric Acid* (IX) : (*i*) *By Wolff-Kishner Reduction.*—The reduction of 17.0 g. of the keto-acid was carried out according to the general procedure of Huang-Minlon (*loc. cit.*), using hydrazine hydrate (85% ; 11.4 g., 2.5 *M*), glycol (85 c. c.) and potassium hydroxide (14.4 g., 3.3 *M*). After the completion of the hydrazone formation (1½ hrs.), the reaction mixture was refluxed for 4½ hours, cooled, diluted with 200 c.c. of water and acidified. The product was purified by distillation and had the constants reported below ; yield 70%.

(*ii*) *By Clemmensen Reduction.*—Freshly powdered zinc (240 g.) was amalgamated in the usual manner and covered with water (150 c. c.), hydrochloric acid (350 c.c.) and toluene (300 c.c.). To this acid (VIII) (80.0 g., m.p. 119-23°) was added, followed by acetic acid (12 c.c.). The reaction mixture was refluxed with stirring for 28 hours and during this period a total of 600 c. c. of hydrochloric acid was added in lots of 100 c. c. at suitable intervals. The product was worked up in the usual manner, and was purified by distillation, when the colorless distillate, b. p. 165°/0.4 mm., solidified at once, m. p. 54°, yield 70.0 g. (90%). A small portion was crystallised from dilute acetic acid, when colorless needles melting at 55° were obtained [Fieser and Seligman, *loc. cit.*, give m. p. as 54.9 - 55.2° (corr.) and report 73% yield].

γ-(5-*Hydrindyl*)-n-*butanol* (X) : (*i*) *By Lithium Hydride Reduction.*—γ-(5-Hydrindyl)-butyric acid (10.2 g., 0.05 *M*) in anhydrous ether (50 c. c.) was added to a solution of lithium aluminium hydride (2.3 g., 0.06 *M*) in ether (50 c. c.) during 15 minutes and then left overnight. The product was worked up in the usual manner (Nystrom and Brown, *loc. cit.*), and was obtained as a colorless, fairly viscous liquid, b. p. 137-38°/0.5 mm., n_D^{24} 1.5400, yield 8.5 g. (89.4%). (Found : C, 82.15 ; H, 9.60. $C_{13}H_{18}O$ requires C, 82.1 ; H, 9.47 per cent).

(*ii*) *By Bouveault-Blanc Reduction.*—Ethyl γ-(5-hydrindyl)-butyrate was prepared in yields of 90-95% by refluxing a solution of the acid (30.6 g., 0.15*M*) in ethyl alcohol (120 c. c.) containing sulphuric acid (6 c. c.) for 12 hours. On working up, the ester was obtained as a colorless, mobile liquid, b. p. 149°/1.3 mm., $n^{27}_{\prime\prime}$, 1.5120; d^{27}_{4}, 1.017; M_D, 68.52 (calc. 67.34; a similar exaltation has been observed in a number of cases, e.g., see Bradfield, Jones and Simonsen, *J. Chem. Soc.*, 1934, 1810). (Found: C, 77.25; H, 8.72. $C_{15}H_{20}O_2$ requires C, 77.58; H, 8 62 per cent).

Bright sodium (15.0 g., 0.65 g. atom; 25% excess) was placed in a dry 3-necked flask, fitted with a Hershberg stirrer (slip-seal), an efficient reflux condenser and a dropping funnel. Sodium was immediately covered with anhydrous toluene (25 c. c.) and heated in an oil-bath at 120° and stirred to somewhat disperse the sodium. A mixture of the above ester (30.16 g., 0.13*M*), anhydrous *tert.*-butyl alcohol (28.8 g., 0.39 *M*) and toluene (100 c. c) was then let in during 45 minutes with stirring. During the exothermic reaction the bath temperature was maintained at 120° ± 5°. After the addition, it was stirred and heated for another 30 minutes, cooled, finally in ice-water and carefully treated with small quantities of ice-water with swirling. When 100 c. c. of water had thus been added the toluene layer was separated and washed with water (30 c. c. × 4). The alkaline washings and previous aqueous portion were combined and extracted with ether (60 c. c. × 3). The combined toluene and ether extracts were washed once with dilute acetic acid (5%) and finally with brine. After drying (Na_2SO_4), the solvents were fractionated off and the product distilled in vacuum, b. p. 137-38°/0.5 mm., n^{27}_D, 1.5370 - 1.5395, yield 22.3 g. (90.2%). (Found: C, 82.31; H, 9.79. $C_{13}H_{18}O$ requires C, 82.1; H, 9.47 per cent).

γ-(5-*Hydrindyl*)-n-*butyl Bromide.*—To the alcohol (X)(44g., 0.232*M*), diluted with anhydrous benzene (30 c. c.), 5 drops of dry pyridine were added and chilled in ice-salt and treated with phosphorus tribromide (21.2 g., 0.078*M*) during 5 minutes and then allowed to attain the room temperature (29°) during 6 hours and then kept at that temperature for 15 hours more. Finallly it was heated at 60°—65° for 1½ hours. It was cooled, poured into ice-water and then extracted with ether (4 times), washed once with water, cold dilute $NaHCO_3$ solution (5%, once) and then again with water and dried (Na_2SO_4). Solvents were distilled off and the residue fractionated from a modified Claisen flask, when the bromide was obtained as a colorless, mobile liquid, b. p. 129°/0.5 mm., n^{30}_D, 1.5490, yield 48 g.(81.9%). (Found: Br, 31.5. $C_{13}H_{17}Br$ requires Br, 31.62 per cent).

γ-(5-*Hydrindyl*)-n-*butyl Cyanide* (XI).—The above bromide (46 g.) in alcohol (Comm., abs., 700 c. c.) was treated with a solution of potassium cyanide (39 g.) in water (155 c. c.). The reaction mixture was heated in the steam-bath for 24 hours and worked up as usual (Heilbron and Wilkinson, *J. Chem. Soc.*, 1930, 423). The nitrile was isolated as a colorless, mobile liquid, b. p. 145-46°/0.5 mm., 155-56°/1 mm, n^{25}_D, 1.5320; yield 33.5 g. (92.7%). (Found: C, 84.0; H, 8.9. $C_{14}H_{17}N$ requires C, 84.4; H, 8.5 per cent).

The residue left after fractionation of the nitrile was taken up in hot benzene; the crystals which separated out on cooling were recrystallised several times from benzene with norit treatment, when colorless, lustrous plates, m. p. 105-106° (yield 1 g.) were obtained. This analysed for the *amide* of the acid (XII). (Found : N, 6.42. $C_{14}H_{19}ON$ requires N, 6.45 per cent.). Cagniant (*loc. cit.*) has recorded the m. p. of the amide as 104°.

δ-(5-*Hydrindyl*)-n-*valeric Acid* (XII) : (*i*) *By Hydrolysis of the Nitrile.*—The nitrile (XI) (33 g.) was refluxed in a solution of potassium hydroxide (22 g. in 22 c.c. of water) in ethylene glycol (110 c.c.) for 18 hours. It was cooled, diluted with water, extracted with ether to remove any neutral material and then acidified with cooling with concentrated hydrochloric acid (Congo red). The precipitated acid was recrystallised by dissolving in alcohol (90 c. c.), clarifying with norit and then diluting with water till just turbid ; the turbidity was removed with a few drops of alcohol and then allowed to crystallise *slowly* during 2 days. The acid was obtained as white needles, m. p. 73-74°, yield 35.2 g. (97%) (Cagniant, *loc. cit.*, gives m. p. 68°). (Found : C, 77.21 ; H, 8.08. $C_{14}H_{18}O_2$ requires C, 77.06 ; H, 8.25 per cent).

(*ii*) *From* (IX) *by Arndt-Eistert Reaction.*—The acid (5.1 g., 0.025*M*) was converted into the acid chloride with PCl_5 (5.8 g., 0.028 *M*) in benzene (5 c. c.) in the usual manner. The acid chloride was isolated as a colorless liquid in 81.0% yield, b. p. 138°/0.65 mm.

The acid chloride (4.45 g., 0.02*M*), diluted with anhydrous ether (5 c. c.), was added dropwise to an ethereal solution of diazomethane (prepared from 10 g. of nitrosomethylurea and 140 c. c. of alcohol-free ether) at −5° with swirling. After 4 hours at room temperature (25°), ether and excess diazomethane were removed under suction at room temperature when the diazoketone was obtained as a viscous yellow liquid, which was taken up in dioxane.

The Wolff rearrangement was carried out by adding (15 mins.) the above solution of the diazoketone dropwise and with stirring to silver oxide (from 10 c. c. of 10% $AgNO_3$ solution) suspended in water (50 c. c.) containing 2 g. of Na_2CO_3, 10 H_2O and 1 g. of $Na_2S_2O_3$ and warmed to 50°-60°. After the addition the reaction mixture was stirred for one hour more, during which period the temperature was slowly raised to 95°. The reaction mixture was worked up in the usual manner and the acid recrystallised (twice) as above, m. p. 73-74° ; mixed m. p. with the above sample remained undepressed ; yield 2.0 g. (46.5% on the acid chloride).

2 : 3 : 6 : 7 : 8 : 9-*Hexahydro*-cyclo*hept*(*f*)-*indene*-5-(1*H*)-*one*(XIII) : (*i*) *By Intramolecular Ring-closure of Acid Chloride.*—The acid (XII) (21.8 g., 0.1*M*) was converted into the acid chloride by PCl_5 (22.8 g., 0.11 *M*) in 125 c. c. of benzene. Benzene and $POCl_3$ were removed under suction at a temperature not exceeding 80°. Last traces of $POCl_3$ were removed by adding 25 c. c. of benzene and then removing it as before. The operation was repeated with two more 25 c. c. portions of benzene and finally with 25 c. c. of CS_2. The acid chloride was then taken up in CS_2 (200 c. c.).

An one-litre flask was fitted up with the dilution apparatus (Cope and Herrick, *loc. cit.*) carrying a dropping funnel and an efficient condenser. Freshly powdered anhydrous $AlCl_3$ (26.7 g., 0.2 *M*) was placed in the flask and covered with purified CS_2 (450 c. c.). The above acid chloride was introduced into the refluxing CS_2 containing the $AlCl_3$ during 42 hours. Refluxing was continued for another 6 hours, after which the solvent was distilled off, the residue treated carefully with ice and hydrochloric acid, and some ether (75 c. c.) added ; the aqueous part was extracted with ether (50 c. c. ×3) and the red ether extracts combined, washed with water (twice) and dilute $NaHCO_3$ solution, again with water (twice) and dried (Na_2SO_4). Ether was distilled off and the residue fractionated to give the ketone (XIII) as a colorless, somewhat viscous liquid, b. p. 139°/0.4 mm., yield 14 g. (72%).

(*ii*) *By Phosphoric Acid-Phosphorus Pentoxide.*—A slurry of phosphorus pentoxide (32 g.) was prepared in syrupy phosphoric acid (85%, 20 c. c.) (Gilmore and Horton, *loc. cit.*). To this was added the acid (XII, 5 g) in one lot, and the deep pink solution, so obtained, was heated on the steam-bath for 2¼ hours and then left overnight. The reaction mixture was added on to ice, the organic material taken up in ether, washed with water, Na_2CO_3 solution (10% ; twice) and again with water. The yellowish ethereal solution, which had a beautiful green fluorescence, was dried, the solvent removed and the residue fractionated to give the ketone in 85.1% (3.9 g.) yield.

The ketone bad n_D^{27}, 1.5785 ; d_4^{27}, 1.0970 ; M_D, 60.54 (calc. 58.88 ; EM_D, 1.66 ; $E\Sigma_D$, 0.83). (Found : C, 83.84 ; H, 7.88. $C_{14}H_{16}O$ requires C, 84.0 ; H, 8.0 per cent).

The 2 : 4-*dinitrophenylhydrazone* was prepared in the usual way (H_2SO_4 method). Crystallisation from benzene (1 part) and alcohol (2 parts) gave bright red, long, flat, shining needles, m. p. 189-90°. (Found : N, 14.81. $C_{20}H_{20}O_4N_4$ requires N, 14.73 per cent).

2 : 3 : 6 : 7 : 8 : 9-*Hexahydro*-cyclo*hept*(*f*)-*inden*-5 (1H)-*ol* (XIV) : (*i*) *By Lithium Aluminium Hydride Reduction.*—To a solution of $LiAlH_4$ (0.285 g., 0.0075*M*) in ether (25 c.c.), the ketone (XIII) (4 g., 0.02 *M.* in 20 c.c. of ether) was introduced over a period of 15 minutes with stirring, such that refluxing of the ether was controlable. After stirring for another 5 minutes, the reaction mixture was refluxed for 10 minutes and then allowed to stand overnight. Excess of the reagent was destroyed by cautiously treating it with water (10 c.c.) and the reaction mixture was chilled in an ice-salt bath and treated with 15% H_2SO_4 (30 c.c.). The crystalline alcohol, started separating out. Sufficient benzene (25 c.c.) was added to dissolve all the solid compound and the solvent layer removed, washed with water (twice) and dried (Na_2SO_4). The solvent was distilled off and the residue recrystallised from dilute alcohol ; yield of the product with m. p. 101-103° was 4 g. (99%) and was quite suitable for the next step.

(*ii*) *By Meerwein-Ponndorf Reduction.*—The ketone (1 g., 0.005 *M.*) was reduced with aluminium *iso*propoxide (5.1 g., 0.025 *M* ; *i.e.* 1400% excess) in anhydrous

*iso*propyl alcohol by the procedure described below for the reduction of benzosuberone. The acetone test was negative after 2 hours, when after refluxing for another 15 minutes, the reaction mixture was poured on to ice and dilute hydrochloric acid, when the alcohol separated as a crystalline solid and was collected by filtration, washed with water and dried, m. p. 101-103°, yield, quantitative.

An analytical sample was recrystallised once from dilute alcohol and again from petroleum ether containing a little benzene, when white, silky needles, m. p. 104.5-105.5° were obtained. The m. p. could not be changed by further recrystallisations. (Found : C, 83.4 ; H, 9.0. $C_{14}H_{18}O$ requires C, 83.16 ; H, 8.91 per cent).

1 : 2 : 3 : 7 : 8 : 9-*Hexahydro*-cyclo*hept* [*f*] *indene* (XV) : (*i*) *Dehydration by* P_2O_5.—The carbinol (XIV) (2.02 g.) was refluxed with phosphorus pentoxide (3 g.) in benzene (20 c. c.) for 2½ hours. The reaction mixture was cooled, diluted with ice-cold water and the benzene layer separated. The aqueous part was extracted with ether and the ether and benzene solutions combined, washed with water and dried (Na_2SO_4). The solvent was distilled off and the residue twice distilled over sodium to give a colorless liquid, b. p. 125-28°/2 mm., n_D^{27}, 1.5935 ; yield 0.6 g. (33%).

(*ii*) *Dehydration over* p-*Toluenesulphonic Acid.*—To the alcohol (XIV) (4.04 g., 0.02 *M.*) in dry benzene (20 c. c.) *p*-toluenesulphonic acid (25 mg.) was added and the reaction mixture refluxed until no more water-benzene azeotrope distilled (45 minutes) (for apparatus see Sukh Dev, this *Journal*, 1953, **30**, 443) ; heating was continued for 15 minutes more, with the benzene distilling off (5 c. c.), *i.e.* not returning to the reaction vessel ; this helped the dehydration to go to completion. If heated unnecessarily longer, the yield of the hydrocarbon decreased owing to its polymerisation. The reaction mixture was cooled, diluted with petroleum ether (40°-60° ; 10 c. c.) and passed it through a column of activated silica gel (-40 mesh ; 50 mm. × 15 mm.). The column was washed with three 10 c. c. portions of petroleum ether. From the eluterate, which was practically colorless, the solvent was stripped off and the residue fractionated over a little sodium, to give the hydrocarbon (XV) as a colorless, quite mobile liquid, b. p. 121-22°/1.1 mm., m. p. 10-10.2°. f. p. 9° ; yield 3.1 g. (84.2%). It had n_D^{27}, 1.5975 ; d_4^{27}, 1.0258 ; M_D, 61.16 (calc. 58.40 ; EM_D, 2.76 ; $E\Sigma_D$, 1.44). (Found : C, 91.0 ; H, 8.78. $C_{14}H_{16}$ requires C, 91.30 ; H, 8.69 per cent).

The hydrocarbon has an odour of *p*-cymene and diphenyl oxide ; it is somewhat unstable and is best stored over a trace of hydroquinone under nitrogen.

A trinitrobenzene complex can be prepared by warming a mixture of the hydrocarbon (202 mg., 0.0011*M*) and T. N. B. (213 mg., 0.001*M*) in alcohol (3 c. c.) for a few minutes and the clear red solution allowed to stand. At first T. N. B. separated out, but on standing (room temp. should be below 23°) and stirring the complex precipitated out with the dissolution of T. N. B. The product was filtered off, an additional amount being obtained from the mother-liquor by cooling in ice ; yield 350 mg., m. p. 65-75°, but became completely fluid at 95°. It was recrystallised several times from alcohol (3 c. c.), to give fine, yellow, silky needles, with the same melting point range ; this was probably due to its dissociation on warming. (Found : N, 10.44, 10.36. $C_{20}H_{19}O_6N_3$ requires N, 10.5 per cent). The complex (700 mg.)

in benzene (5 c. c.) was passed through a column of alumina (15 g., 12 cm. ×1.5 cm ; activity I), which was washed with petroleum ether (10 c. c.×3). From the combined eluterates, the solvent was distilled off and the regenerated hydrocarbon distilled, b. p. 132°/2.8 mm., n_D^{28}, 1.5970, yield 320 mg.

1 : 2 : 3 : 7 : 8 : 9-*Hexahydro*-5-*methyl*cyclo*hept*[*f*]-*indene* (XVI).—The ketone (XIII) (2 g., 0.01 *M*), dissolved in dry ether (20 c. c.), was added to a solution of methylmagnesium iodide, prepared from magnesium (0.2 g., 0.012 *M*), methyl iodide (2.8 g., 0.02*M*) and ether (20 c. c.). After keeping in the ice-bath for one hour, it was left aside at room temperature for 12 hours and then refluxed for 3 hours. It was worked up with ammonium chloride and ice in the usual manner and the crude carbinol (2.1 g.), thus obtained, was dehydrated with formic acid (90% ; 5 c. c., 2 hrs. on a steam-bath) and the hydrocarbon isolated and purified by distillation over sodium to give a colorless, slightly viscous liquid, b. p. 128°/0.5 mm., n_D^{27}, 1.5770, yield 1.4 g. (71%). (Found : C, 91.04 ; H, 9.27. $C_{15}H_{18}$ requires C, 90.90 ; H, 9.09 per cent).

Attempted Dehydrogenations.—In a typical experiment designed to dehydrogenate (XV), the hydrocarbon (0.9 g.) was passed during 10 hours at 35 mm. (nitrogen atmosphere) through a catalyst bed (55 mm.) consisting of 10% Pd-C (0.5 g.) and activated alumina (−10,+20 mesh ; 0.5 g.) and heated to 330°-340°. (For apparatus see Sukh Dev, this *issue*, Part II, p. 729). The "distillate" (600 mg.) was colorless and had n_D^{24}, 1.5930 ; it was chromatographed over alumina, using petroleum ether for elution, when various fractions with n_D^{21}, 1.5530-1.5970 were obtained, but none showed the behaviour expected of a system (V).

5-*Hydroxybenzosuberan* ("*Benzosuberol*")

(*i*) *By Lithium Aluminium Hydride Reduction.*—Benzosuberone (Gilmore and Horton, *loc. cit.*) (3.2 g., 0.02 *M* ; in 25 c.c. of anhydrous ether) was introduced dropwise into a suspension of $LiAlH_4$ (0.285 g., 0.0075 *M*) with magnetic stirring. A white, powdery complex started separating. After the addition was complete (5 mins.), the product was stirred for another ten minutes and then left overnight (15 hours). Finally it was refluxed for 15 minutes and worked up as usual. The product was recrystallised from dilute alcohol to give white, silky needles, m.p. 102-103°, yield 3.2 g. (98.7%).

(*ii*) *By Meerwein-Ponndorf Reduction.*—Benzosuberone (16.0 g., 0.1 *M*), aluminium *iso*propoxide (40.8 g., 0.2 *M* ; 500% excess) and anhydrous *iso*propyl alcohol (150 c.c.) were placed in a flask (300 c.c.), to which an one-foot vigreous column with a total-condensation variable take-off-type still head was attached. The reaction mixture was gently refluxed under total condensation and five minutes later the distillate was collected at a rate of 1-5 drops/minute. The thermometer registered 63°-66° during the first 2½ hours and then the temperature slowly rose to 73°-75° and finally to 80°. The acetone test was negative after 15 hours, when the reaction mixture was cooled, and added on to cold dilute hydrochloric acid (70 c.c. HCl, 175 c.c. water and 175 g. ice). When all the aluminium salts had gone in solution,

water (150 c.c.) was added and the crystalline carbinol collected, washed with water and dried, m.p. 101-102°, yield quantitative. The product was recrystallised from dilute alcohol (alcohol, 8 c.c.), when white, silky needles, with a fruity odour were obtained, m.p. 103-103.5° (constant); yield 16.0 g. (98.7%). A small portion was sublimed at 95°/30 mm., m.p. 100° and the product had a little off-odour. Horn and Rapson (*loc. cit.*) report m.p. as 101°.

3 : 5-*Dinitrobenzoate* was prepared in the usual manner and crystallised thrice from a mixture of benzene and petroleum ether to give white, thick prisms, m.p. 79-80°. (Found : N, 7.83. $C_{18}H_{16}O_6N_2$ requires N, 7.86 per cent).

An *Oppenauer oxidation* was carried out by refluxing the alcohol (1.63 g., 0.01 *M*) in dry benzene (25 c.c.) in the presence of dry acetone (23.2 g., 0.4 *M*) for 20 hours. The product was cooled, treated with dilute sulphuric acid (5%, 50 c.c.); the benzene layer was separated, washed once with water and dried. The residue left on removal of the solvent gave two fractions on rectification : (*i*) b.p. 86°-87°/3.5 mm., n_D^{27}, 1.5800; yield 0.6 g. (*ii*) b.p. 116°/3.5 mm., n_D^{27}, 1.5660; yield 0.6 g. The fraction (*i*) consisted essentially of the dehydration product (see below), while (*ii*) was identified as benzosuberone through the 2 : 4-dinitrophenylhydrazone (m.p. 210.5°).

1 : 2-*Benzo*-$\Delta^{1:3}$-cyclo*heptdiene* (*Benzosuberene*).—Benzosuberol (8.1 g., 0.05*M*), benzene (dry, 4 c.c.) and *p*-toluenesulphonic acid (150 mg.) were refluxed till no more water separated (45 mins.). The reaction was continued for another 15 minutes as described under the preparation of (XV, *ii*). The cooled reaction mixture was diluted with petroleum ether (20 c.c) and the dark coloured solution passed through a column of activated silica gel (-40 mesh ; 50 mm.×15 mm.), which was then washed with three 15 c.c. portions of the same solvent. The combined eluterate (light yellow) was distilled to remove the solvent and the residue fractionated over a trace of sodium to yield the hydrocarbon as a colorless, mobile liquid, b.p. 96°/7 mm., n_D^{25}, 1.5855, yield. 6.4 g. (88.8%). An analytical sample had n_D^{29}, 1.5840; d_4^{29}, 0.9942; M_D, 48.46 (calc. 46.74; EM_D, 1.72; $E\Sigma_D$, 1.19). Horn and Rapson (*loc. cit.*) give b.p. 108°110°/18 mm., $n_D^{19.5}$, 1.5873. (Found : C, 91.59; H, 8.40. Calc. for $C_{11}H_{12}$: C, 91.66; H, 8.33 per cent).

It did not yield any complex with T.N.B. (cf. behaviour of XV).

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SEARCH FOR NEW INSECTICIDES. PART VII

By A. B. Sen and S. S. Parmar

Several *p*-chlorobenzyl ethers of 2-alkylthymols have been prepared and the results of the bio-assay of their insecticidal activity recorded.

In a previous communication (Sen and Parmar, this *Journal*, 1953, **30**, 59) the preparation of a number of *o*-chlorobenzylaryl and allylaryl ethers of halophenols has been described. In this paper the preparation of a number of *p*-chlorobenzylaryl ethers of 2-alkylthymols has been described in view of the fact that they contain a neurotoxic haloaryl group and an ether linkage having lipophilic property, the two factors necessary for a good contact insecticide (Tien-Chin Chen and Sumerford, *J. Amer. Chem. Soc.*, 1951, **73**, 4694). In addition to this the presence of a halogen atom as a *para* substituent also contributes towards the insecticidal activity of the compounds (Stephensen and Waters, *J. Chem. Soc.*, 1946, 339). The 2-alkylthymols were prepared by Clemmensen reduction of the *o*-hydroxyketones obtained by the Fries rearrangement of the appropriate thymyl esters (Sen, Tewari and Parmer, this *Journal*, 1952, **29**, 407). The 2-alkylthymols, thus obtained, were converted into the corresponding *p*-chlorobenzyl ethers by refluxing the mixture of the appropriate alkylphenol with equivalent amounts of *p*-chlorobenzyl bromide and potassium hydroxide in 95% ethanol for 5 to 6 hours by following the method of Tien-Chin Chen and Sumerford (*loc. cit.*). The testing of the insecticidal activity of the compounds has been exclusively against *Musca nebulo*, laboratory bred and five days old, which conform to the standard knock down tests for evaluating the insecticidal activity.

Experimental

2-Alkylthymols were prepared in the usual manner from the *o*-hydroxyketones (Sen, Tewari and Parmar, *loc. cit.*) through the use of amalgamated zinc and hydrochloric acid, as described for the preparation of alkylcarvacrols (Sen and Parmar, this *Journal*, 1953, **30**, 61). 2-Alkylthymols, thus obtained in yields ranging from 54 to 07%, are recorded in Table I.

Table I

[R = thymyl. K = ketone]

Ketone.	Alkylphenol.	B.P.	Yield.	Mol. formula.	Carbon.		Hydrogen.	
					Found.	Calc.	Found.	Calc.
R-ethyl-K	R-*n*-propyl	113°/5mm.	54.89%	$C_{13}H_{20}O$	81.01	81.24	10.12	10.42
R-*n*-propyl-K	R-*n*-butyl	119°/4	54.26	$C_{14}H_{22}O$	81.07	81.55	10.30	10.68
R-*n*-butyl-K	R-*n*-amyl	159°/9	55.31	$C_{15}H_{24}O$	81.55	81.82	10.72	10.91
R-*n*-amyl-K	R-*n*-hexyl	145°/6	57.24	$C_{16}H_{26}O$	81.83	82.05	10.94	11.11
R-*n*-hexyl-K	R-*n*-heptyl	163°/5	67.60	$C_{17}H_{28}O$	81.91	82.26	11.01	11.29
R-*n*-heptyl-K	R-*n*-octyl	166°/5	63.2)	$C_{18}H_{30}O$	82.05	82.45	11.12	11.45
R-*n*-undecyl-K	R-*n*-dodecyl	177°/5	60.01	$C_{22}H_{36}O$	82.70	83.01	11.76	11.95
R-*n*-tridecyl-K	R-*n*-tetradecyl	191°/5	62.41	$C_{24}H_{42}O$	82.91	83.23	11.98	12.14

p-*Chlorobenzyl bromide* was prepared by the bromination of *p*-chlorotoluene with N-bromosuccinimide in the presence of a small amount (0.5g.) of benzyl peroxide as a catalyst (Schmid and Karrer, *Helv. Chim. Acta*, 1946, **29**, 573), yield 72.7%, b. p. 115°/10 mm., m.p. 48° (lit. m. p. 48.5°.)

p-*Chlorobenzyl ethers* of 2-alkylthymols were prepared by following the method of Tien-Chin Chen *et al.* (*loc. cit.*). KOH(0.1*M*) was dissolved in 50 c. c. of 95% ethanol to which alkylphenol (0.1*M*), dissolved in 10 c.c. of 95% ethanol, was added. Now to this *p*-chlorobenzyl bromide (0.1*M*) was added and the mixture refluxed on the water-bath for 5 to 6 hours until KBr ceased to separate. The potassium bromide was removed by filtration and the alcoholic solution was poured over chipped ice when the ethers separated as oils. The ethers, thus obtained, were extracted with ether and the ethereal solution was washed successively with 10% caustic soda solution and water. The ether extract was dried over anhydrous sodium sulphate. After removal of the solvent the residual oil was distilled under reduced pressure. The *p*-chlorobenzyl ethers, thus obtained in yields ranging from 52 to 68%, are recorded in Table II.

TABLE II

p-Chlorobenzyl ether.
[t=thymol].

Alkylphenol.	B. P.	Yield.	Mol. formula	Carbon.		Hydrogen.	
				Found.	Calc.	Found.	Calc.
2-*n*-Propyl-t	125°/5 mm.	60.64%	$C_{20}H_{25}OCl$	75.45	75.81	7.72	7.90
2-*n*-Butyl-t	141°/5	59.54	$C_{21}H_{27}OCl$	75.90	76.25	8.02	8.18
2-*n*-Amyl-t	151°/6	63.16	$C_{22}H_{29}OCl$	76.25	76.63	8.12	8.42
2-*n*-Hexyl-t	175°/6	56.16	$C_{23}H_{31}OCl$	76.57	76.98	8.38	8.65
2-*n*-Heptyl-t	178°/6	56.16	$C_{24}H_{33}OCl$	76.95	77.31	8.62	8.86
2-*n*-Octyl-t	180°/5	54.22	$C_{25}H_{35}OCl$	77.33	77.60	8.76	9.06
2-*n*-Dodecyl-t	189°/6	52.82	$C_{29}H_{43}OCl$	78.41	78.65	9.61	9.72
2-*n*-Tetradecyl-t	185°/4	57.69	$C_{31}H_{47}OCl$	78.87	79.05	9.62	9.99

Bio-assay of the Insecticidal Action.—The tests have been exclusively against *Musca nebulo* (laboratory bred and five days old). For this purpose solutions in mineral oil were prepared containing 1% of the active ingredient in each case (w/v). In each case 0.2 c.c. of the solution was sprayed under identical conditions by means of a special applicator against 20 houseflies encased in a glass jar and covered under mosquito netting. After application of the insecticides, time intervals were noted in each case for 50% knock down and 100% knock down. Whenever no knock down could be noticed even in 60 minutes, the particular test was abondoned. In certain instances,

however, when a slow insecticidal activity was noticed, the test was extended up to two hours. For the purpose of comparison the results were carried out *pari passu* with :

(*i*) 1% DDT (75% *pp'*- isomer)
(*ii*) 1% BHC Technical (13/14% γ-isomer)
(*iii*) 0.01% Pyrethrin I+II.

The results are summarised in Table III.

TABLE III

No.	Compounds.	Biological test. 50% K. D. min.	100% K. D. min.
1.	*p*-Chlorobenzyl ether of 3-methyl-2-*n*-propyl-6-*iso*propyl phenol	No. K. D. for 60 mins.	
2.	*p*-Chlorobenzyl ether of 3-methyl-6-*iso*propyl-2-*n*-butyl phenol	No. K. D. for 60 mins.	
3.	*p*-Chlorobenzyl ether of 3-methyl-6-*iso*propyl-2-*n*-amyl phenol	No. K. D. for 120 mins.	
4.	*p*-Chlorobenzyl ether of 3-methyl-6-*iso*propyl-2-*n*-hexyl phenol	62	98
5.	*p*-Chlorobenzyl ether of 3-methyl-6-*iso*propyl-2-*n*-heptyl phenol	64	>120
6.	*p*-Chlorobenzyl ether of 3-methyl-6-*iso*propyl-2-*n*-octyl phenol	No K. D. for 120 mins.	
7.	*p*-Chlorobenzyl ether of 3-methyl-6-*iso*propyl-2-*n*-dodecyl phenol	51	91
8.	*p*-Chlorobenzyl ether of 3-methyl-6-*iso*propyl-2-*n*-tetradecyl phenol	No K. D. for 120 mins.	
	1% DDT (75% *p p'*-isomer)	6	11
	1% BHC Technical (13/14% γ-isomer)	4	7
	0.01% Pyrethrin I+II	33 sec.	71 sec.

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804